

ELEMENTAL ASSESSMENT AND EXTRACTION OF THE WASTE ROCK TAILINGS FROM A FREE STATE GOLDMINE

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Declaration by candidate

I declare that the work presented in this dissertation, submitted for the Master of Science in Chemistry, at the University of the Free State is my original work and has never been submitted at any other institution previously. Furthermore, I declare that the quoted sources in this work have been acknowledged by means of references.

Signature_____

Lijo Pius Mona

Date _____

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LIST OF ABBREVIATIONS

Instruments/ techniques:

| | |
|---------|---|
| ICP-OES | Inductively Coupled Plasma-Optical Emission Spectroscopy |
| ICP-MS | Inductively Coupled Plasma Mass Spectrometry |
| SEM-EDS | Scanning electron microscopy energy dispersive x-ray spectroscopy |
| IEC | Ion exchange chromatography |
| AAS | Atomic absorption spectroscopy |

Statistical abbreviations:

| | |
|-----|-----------------------------|
| LOD | Limit of detection |
| LOQ | Limit of quantification |
| SD | Standard deviation |
| RSD | Relative standard deviation |

KEYWORDS

Mine waste

Waste rock

Tailings

Mine water

Acid mine drainage

Beneficiation

Recovery

Precipitation

Samples

Dissolution

Concentrations

1 BACKGROUND AND MOTIVATION OF STUDY

1.1 INTRODUCTION

Mine waste is the product of mining activities which have taken place over decades and centuries. Waste products include the solid, liquid and gaseous by-products which are generated during the mining of the ore and the subsequent processing of ores and minerals to the desired products.^{1,2} The major types of mine waste include waste rock, tailings and mine waste water. Waste rocks consist of either unmineralised rocks or rocks that are too low in concentrations of elements of interest for commercial beneficiation.³ Additionally, they could comprise minerals which are of no economic interest to the mine and include the mine wall rocks which are removed to access the target ore. **Figure 1.1**² represents an illustration of a typical underground mine showing the ore-body. In this case, the area shaded in grey is the position of origin of waste rock as is the area shaded in black which is open into underground passages leading to the ore-body. Rocks from any part of the surroundings of the ore-body may likewise form part of the waste rock. These rocks may be further divided into overburden (produced at the mine surface) and mine development rocks (product of extraction of ores in underground mines).⁴ Mine tailings (slurry), on the other hand, are a mixture of crushed rock and processing fluids and are produced during transformation of an ore to a product of a higher

¹ Mining waste management. [Accessed 12-01-2017]. Available at:

https://books.google.co.za/books?id=P_S-V7WYfPYC&printsec=frontcover#v=onepage&q&f=false

² B. G. Lottermoser. (2007). Mine wastes: characterization, treatment, environmental impacts, 3rd ed. New York: *Springer*, pp.3-6

³ D. E. Daniel. (1996). Geotechnical practice for waste disposal, 3rd ed. Dordrecht: *Springer*, p.271

⁴ R. Das, I. Choudhury. (2013). "Waste management in mining industry", *Indian Journal of Scientific Research*, 4(2), pp.139-142

value, for either local consumption or for exportation at a higher price.⁵ Mine water is the surface and ground water that enters mining excavations during mining operations.⁶

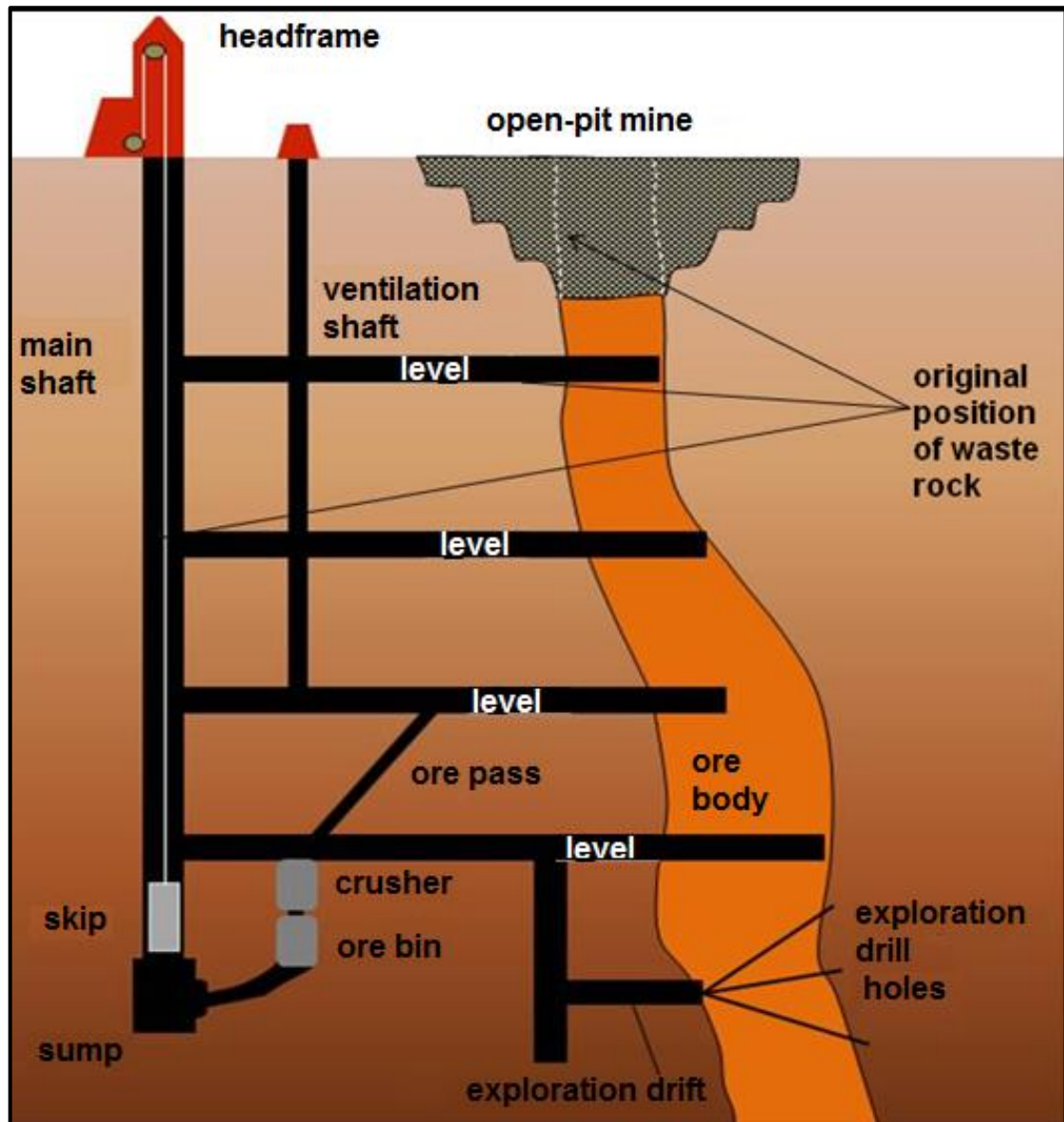


Figure 1.1: Schematic presentation of an underground mine⁷

⁵ D. Kossoff, W. E. Dubbin. (2014). "Mine tailings dams: Characteristics, failure, environmental impacts, and remediation", *Applied Geochemistry*, 51, pp.229-245

⁶ Mine water. [Accessed 25-03-2017]. Available at :
<http://encyclopedia2.thefreedictionary.com/Mine+Water>

1.2 STORAGE, OCCURRENCE, ENVIRONMENTAL AND HEALTH IMPACTS

Waste is normally stored in dumps and dams close to the mine site for a long time (up to 200 years).⁸ Tailings may be stored under water in what is called tailings ponds to prevent surface dust and acid mine drainage formation. If the waste contains high concentrations of sulphide minerals, waste rock may also be stored under water, due to the high potential for acid rock drainage.⁵ A typical mine waste dump is depicted in **Figure 1.2**. Advantages of this type of storage include easy access to the waste which can be reused or recycled (for example, for filling up the pit in the case of mine closure) and easy management of the waste.^{9,10} Tailings may be leached or reprocessed to beneficiate more of the valuable elements. Waste rock may be utilised for construction of roads and dams, paving, to obtain fine and coarse concrete and in the manufacturing of construction bricks.¹¹

Disadvantages of piling waste as depicted in **Figure 1.2** include the generation of environmental hazards such as acid release during a leaching process throughout the rainy season, radiation build-up if the waste contains naturally occurring radioactive metals (NORMs) like uranium, thorium, and radon.¹² Moreover, surface

⁷ Metal deposits. [Accessed 13-02-2018]. Available at:

[https://geo.libretexts.org/Textmaps/Map%3A_Physical_Geology_\(Earle\)/20%3A_Geological_Resources/20.1%3A_Metal_Deposits](https://geo.libretexts.org/Textmaps/Map%3A_Physical_Geology_(Earle)/20%3A_Geological_Resources/20.1%3A_Metal_Deposits)

⁸ G. Blight. (2010). *Geotechnical engineering for mine waste storage facilities*, London, UK: *Taylor & Francis Group*, p.12

⁹ How are waste materials managed at mine sites. [Accessed 14-03-2017]. Available at: <http://www.miningfacts.org/Environment/How-are-waste-materials-managed-at-mine-sites/>

¹⁰ W. J. Rankin. (2011). *Minerals, metals and sustainability: meeting future needs*, Australia: *CSIRO Publishing*, pp.245-246

¹¹ Z. Lu, M. Cai. (2001). "Disposal methods on solid wastes from mines in transition from open-pit underground mining", *Procedia Environmental Sciences*, 16, pp.715-721

¹² M. Foulkes, G. Millward, S. Henderson, W. Blake. (2017). "Bioaccessibility of U, Th and Pb in solid wastes and soils from an abandoned uranium mine", *Journal of Environmental Radioactivity*, 173, pp.85-96

and ground water resources can be contaminated by elements present in the waste material such as iron, manganese, zinc, lead and arsenic from acid leaching of the waste.¹³



Figure 1.2: Illustration of a mine waste dump¹⁴

Mining is a global activity as may be observed in **Figure 1.3**¹⁵ which illustrates the places where active mining is taking place, and, as expected, many places or sites worldwide where mine waste is generated. The global total mine waste produced per annum is not known. However, the ratio of the waste to the target element is very high. For example, production of one ton of copper yields about 99 tons of waste. The ratio is even higher for gold, as production of a ton of gold yields about 200 000 tons of tailings.¹⁵ Considering these ratios and the massive rates of mineral production globally, it is evident that the rate of mine waste production is extremely high.

¹³ M. Mujuru, S. Mutanga. (2016). Management and mitigation of acid mine drainage in South Africa, 1st ed, Pretoria, *Africa Institute of South Africa*, p.42

¹⁴ Mine waste dump. [Accessed 16-02-2017]. Available at:

<https://www.google.co.za/imgres?imgurl=https%3A%2F%2Fi.ytimg.com%2Fvi%2F3NPxpxvOMSI%2Fmaxresdefault.jpg&imgrefurl=https%3A%2F%2Fwww.youtube.com%2Fwatch%3Fv%3D3NPxpxvOMSI&docid=HSq9Q2njbckISM&tbnid=gY6eVmpwtcvBYM%3A&vet=1&w=1920&h=1080&bih=765&biw=811&q=mine%20waste%20dump&ved=0ahUKEwiD7Ibp0KDSAhWCDcAKHYdSDjkQMwgfKAAwAA&iact=mrc&uact=8>

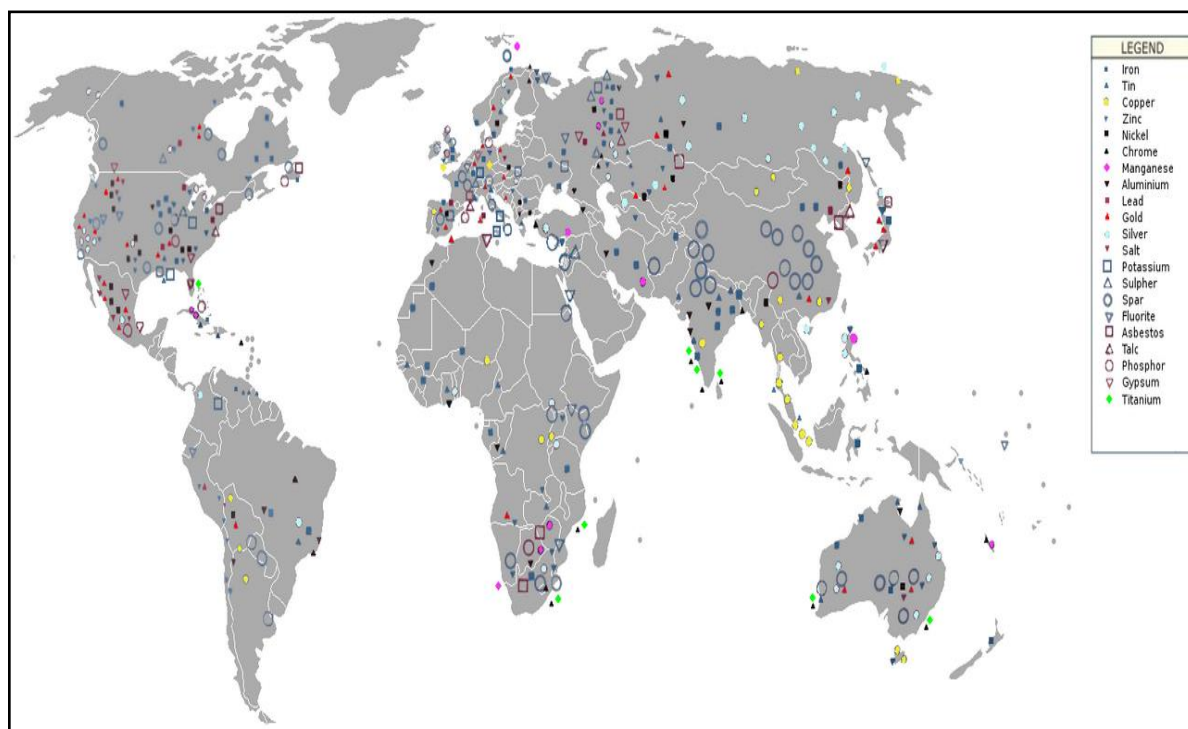


Figure 1.3: Simplified world active mining map¹⁵

There are several health problems which may be directly or indirectly attributed to human exposure to mine waste. These include the generation of acid mine drainage which can contaminate water bodies used by humans, which is produced when sulphide minerals react with water and oxygen in the air to produce sulphuric acid¹⁶ and the resulting acid water which drains from the mine sites can be very concentrated (up to 300 times as concentrated as acid rain). The acidic drainage can destroy aquatic life¹⁷ or leach heavy metals, such as arsenic from the ore bodies, which contaminate water sources, particularly rivers and streams. It is well known that arsenic can cause tumours and skin cancer, while lead can cause learning disabilities and impaired child development, and an element such as cadmium is likely to cause liver diseases.¹⁷ Cyanide, which is used to extract gold from its ores,

¹⁵ Mining. [Accessed 02-05-2016]. Available at: <https://en.wikipedia.org/wiki/Mining>

¹⁶ K. K. Kefeni, T. A. M. Msagati, B. B. Mamba. (2017). "Acid mine drainage: Prevention, treatment options, and resource recovery: A review", *Journal of Cleaner Production*, 151, pp.475-493

¹⁷ P. Zhuang, M. B. McBride, H. Xia, N. Li, Z. Li. (2009). "Health risk from heavy metals via consumption of food crops in the vicinity of Dabaoshan mine, South China", *Science of The Total Environment*, 407(5), pp.1551-1561

may end up in leach ponds which can destroy the surrounding fauna and flora¹⁸ while human consumption of the contaminated water resources can have disastrous effects. However, the cyanide may be converted to the less toxic cyanate form by natural or biological oxidation. It may also be removed by natural volatilisation.¹⁹ The dust which originates from mine waste poses a risk of silicosis to human beings living near the mines.

1.3 MOTIVATION OF THE STUDY

The most pressing challenge for mine management is the proper disposal and management of mine wastes to ensure the smallest impact on the environment, humanity and organisms living around the mine sites. On the contrary, the mine waste can be a very useful resource for the recycling and extraction of other important elements than those which were initially targeted by the miners who went before. A huge advantage of the processing of waste for other important elements is its availability on the surface with little or no additional costs required for the mining of these resources. It is, therefore, important to evaluate the chemical composition of the waste for reprocessing purposes or for limiting its effect on the environment. For those elements which were not important initially or unprofitable to mine, but which are lying on the surface, it is important to find better and/or improved hydrometallurgical processes for upgrading and the extraction of such elements. Of greater significance are the tailings, which may contain different poisonous or harmful elements that are left behind after the initial processing steps and may include heavy

¹⁸ Mining. [Accessed 15-02-2017]. Available at:

<http://web.mit.edu/12.000/www/m2016/finalwebsite/problems/mining.html>

¹⁹ R. Alvarez, A. Ordonez, T. Martinez, J. Lored, F. Pendas, P. Younger. Passive treatment for the removal of residual cyanide in drainage from closed gold mine tailing ponds. [Accessed 20-02-2018]. Available at: https://www.imwa.info/docs/imwa_2004/IMWA2004_38_Alvarez.pdf

and radio-active metals from deep mine activities.²⁰ It is also known, moreover, that both waste rock and tailings may give rise to acid mine drainage.

1.4 AIM OF THE STUDY

Bearing in mind the motivation above, the following objectives were identified for the study:

- To investigate the elemental composition of the waste rock dumps and tailings in order to identify any valuable elements that may be present
- To identify suitable dissolution methods for the different solid waste products
- To determine the concentrations of the identified elements in the waste
- To analyse the drainage water or dry drainage bed alongside the dumps in order to investigate possible leaching of metals from the dumps into the streams
- Investigation of different techniques for the beneficiation of some of the valuable metals present in the waste samples.

²⁰ M. N. Rashed. (2010). "Monitoring of contaminated toxic and heavy metals, from mine tailings through age accumulation, in soil and some wild plants at Southeast Egypt", *Journal of Hazardous Materials*, 178(1-3), pp.739-746

2 THE BACKGROUND OF GOLD MINE WASTE IN SOUTH AFRICA

2.1 INTRODUCTION

Global mining activity produces vast and ever-increasing quantities of waste, due to consumer demands and worldwide economic development and growth.²¹ With the high and increasing demand for mineral commodities, the number of active mines around the world is expected to increase, and the amount of waste is also expected to rise accordingly. There are numerous abandoned waste facilities from earlier mining activities which compound the global waste dilemma. More often than not, the bulk of the waste products at mines have culminated from the mineral processing activities that take place near the mining sites. These activities include the extraction of the ore from the earth and its processing, which includes the crushing, dissolution (hydro- or pyrometallurgical), separation and isolation of elements of interest to economically valuable concentration and/or the production of the elements of interest.

Gold was first discovered in South Africa at the Witwatersrand region in 1884, followed by the establishment of the first large mining company in 1886.²² Since then, the gold mining industry has grown tremendously and has contributed significantly to the economy and the development of infrastructure in the country. In 2007, the industry employed more than 240 000 people and generated R49 billion in

²¹ Mining waste set to grow, but 'reduce, reuse, recycle' solutions abound. [Accessed 09-04-2019]. Available at: <http://www.engineeringnews.co.za/article/mining-waste-set-to-grow-but-reduce-reuse-recycle-solutions-abound-2018-09-07-1>

²² Discovery of gold in 1884. [Accessed 09-05-2018]. Available at: <https://www.sahistory.org.za/article/discovery-gold-1884>

foreign currency earnings.²³ The Witwatersrand basin still holds the largest gold reserve in the world, and mining in this region has already produced over 40 000 tonnes of gold, which is equivalent to about 50% of all the gold ever mined across the world.²⁴

Mining of gold deposits in the Welkom area, in the Free State province, dates back to 1933. Since 1939 (when the major mining activities started) up to the present times, the exploitation of minerals in the area has been intensive.²⁵ Recently, numerous mines in the area closed down, leaving behind a number of abandoned mines and huge dumps of mine waste. The abandoned mines are already being abused and have resulted in many fatal accidents, and crimes perpetrated by illegal miners. Moreover, the mine waste dumps tarnish the natural environment and have the potential to liberate potentially harmful elements capable of contaminating local natural resources such as water and air (see **Chapter 1, Section 1.2**). However, the same waste can also be a source of other valuable elements which were mined simultaneously with the Au, but were deemed to be of no economic importance by the previous mine houses.²⁶

Different types of waste are generated during all the mining activities, which include solid, liquid and even gaseous products. The solid waste produced from these activities may range in particle size from boulders to fairly fine particles. The liquid waste which is produced is the result of hydraulic washing and leaching/dissolution of the ore. This liquid waste is generally discharged together with fine solid particles as slurry and stored in the dumps close to the mines. Airborne waste may include respirable dust particles²⁷ and fumes, some of them harmful, which are released

²³ Gold mining in South Africa. [Accessed 09-05-2018]. Available at: <https://www.projectsia.co.za/gold-mining-in-south-africa.htm>

²⁴ Witwatersrand basin. [Accessed 09-05-2018]. Available at: https://en.wikipedia.org/wiki/Witwatersrand_Basin

²⁵ Welkom, [Accessed 07-05-2018]. Available at: <https://en.wikipedia.org/wiki/Welkom>

²⁶ C. Rampacek. (1982). "An overview of mining and mineral processing waste as a resource", *Resources and conservation*, 9, pp.75-86

²⁷ A. R. Zota, R. Willis, R. Jim, G. A. Norris, J. P. Shine, R. M. Duvall, L. A. Schaidler, J. D. Spengler. (2009). "Impact of mine waste on airborne respirable particulates in northeastern Oklahoma, United States", *Journal of the air and waste management association*, 59(11), pp.1347-1357

from the processing plants.²⁸ The discharge of this solid waste has been found to play a significant role in causing several airborne diseases to the communities residing in the vicinity of mines (see **Figure 2.1**) as a result of fine dust particles being blown from the waste.²⁹



Figure 2.1: Gold mine waste dumps close to a residential area³⁰

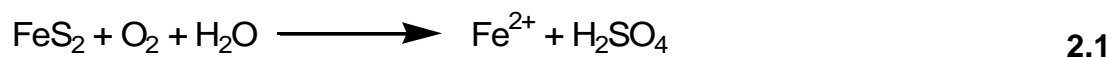
²⁸ Mining and health. [Accessed 31-03-2018]. Available at:

http://hesperian.org/wp-content/uploads/pdf/en_cgeh_2012/en_cgeh_2012_21.pdf

²⁹ P. C. S. Coelho, J. P. F. Teixeira, O. N. B. S. M. Goncalves. (2011). "Mining activities: health impacts", *Encyclopedia of environmental health*, pp.788-802

³⁰ K. Bobbins, G. Tangos. (2018). *Mining landscapes of the Gauteng city-region* research report no. 07, Gauteng city-region observatory (GCRO), p.63

An added ecological or environmental problem is represented by the secondary pollution processes that occur when the waste is exposed to the environment. When the solid waste (normally containing pyrite), for example, is exposed to water and atmospheric oxygen, the result is the formation of acidic water as indicated in **Equation 2.1**.³¹



The resultant acidic water has the potential further to leach heavy metals and other harmful chemicals from the waste dumps into the natural water bodies (**Figure 2.2**) around the waste dumps or sites. The contamination of these surface and ground water bodies is of great concern to the natural environment and detrimental to the health of the communities who live close to these water bodies. Ingestion of this water, directly or indirectly, has the potential to cause a range of harmful to fatal diseases in humans, animals and plants and to the overall degradation and deterioration of the immediate environment.



Figure 2.2: Acid mine drainage contaminated with leached metals³¹

³¹ Acid Mine Drainage Visual Environmental Education Guide. [Accessed 03-11-2017]. Available at: https://www.bucknell.edu/Documents/EnvironmentalStudies/Acid_Mine_Drainage.pptx

Moreover, radiation from radioactive elements within the waste present in the waste sites can also adversely impact communities and animals with the potential of mutation in new-born, or cancer.³² Radiological analyses of the gold tailings in Gauteng were carried out in 2016 by the use of gamma spectroscopy. It was found that the tailings had radiation from ^{238}U , ^{232}Th and ^{40}K of average activities 785.3 ± 13.7 , 43.9 ± 1.0 and 427.0 ± 13.1 Bq/kg respectively.³³ The average activities from a control area were found to be 17.0 ± 0.4 , 22.2 ± 0.5 and 496.8 ± 15.2 Bq/kg for ^{238}U , ^{232}Th and ^{40}K ; respectively. From these radiological measurements, it is clear that the contribution by ^{238}U is much higher than the control, thus illustrating the contribution of mining activities to the increase in environmental radioactivity.

In this chapter, the generation of different types of waste during gold mine activities is dealt with. The chapter covers some of the processes involved in the beneficiation of the gold in the virgin ores, since the information may facilitate an appreciation and understanding of the potential composition of the waste and of the chemistry of the waste in relation to the composition of waste that is generated at the gold mines.

The chapter moreover deals with potential routes or processes in which the waste may be used or recycled to recover other valuable elements for beneficiation. This may turn what may be viewed as a waste and ecological problem, into a valuable elemental resource which may be used as a raw material for the recovery of valuable elements. Although environmental considerations are not the main aim of the study, they are addressed while the main objective focused on is the evaluation of the potential economic value in the readily available waste materials scattered around some of the gold mines in South Africa.

³² G. Wendel. (1998). "Radioactivity in mines and mine water - sources and mechanics", *The journal of the South African institute of mining and metallurgy*, (2), pp.87-92

³³ C. Kamunda, M. Mathuthu, M. Madhuku. (2016). "An assessment of radiological hazards from gold mine tailings in the province of Gauteng in South Africa", *International journal of environmental research and public health*, 13(1), pp.138-147

2.2 TYPES AND GENERATION OF MINE WASTE

In the mining industry, wastes are produced mainly during the extraction, beneficiation and processing of the minerals. The main types of mine waste are waste rock, tailings, and mine water. The first step in the development of any mine is the excavation of the top soil/rock layers, in some instances up to depths of 4 km,³⁴ to reach the mineral reefs rich in gold. The process involves the digging and removal of gangue from the Earth's crust by blasting, which produces waste rock, which may be further classified into overburden and mine development rock.³⁵ Overburden is a result of the development of surface mines while mine development rock is a by-product of the extraction of minerals in underground mines. Mine rock waste is normally dumped at nearby sites and the dumps are heterogeneous in terms of structure and grain-size (**Figure 2.3**). In a waste dump, coarse materials tend to settle towards the base while finer materials remain at the top of the dump.³⁶

³⁴ C. R. Speers, A. J. S. Spearing. (1996). "The design of tunnel support in deep hard-rock mines under quasistatic conditions", *The journal of the South African institute of mining and metallurgy*, 96(6), pp.47-54

³⁵ R. Das, I. Choudhury. (2013). "Waste management in mining industry", *Indian Journal of Scientific Research*, 4(2), pp.139-142

³⁶ Mine Waste dumps and tailing dams. [Accessed 01-05-2017]. Available at: <https://www.coursehero.com/file/15284738/12-Mine-Waste-dumps-and-tailing-damspdf/>



Figure 2.3: Mine waste rock dump showing heterogeneity in grain size³⁷

A comparison of the quantity of process waste to that of the mineral processed, during the production of a sought after/desired element, gives an estimate of the quantity of waste rock produced over a certain period of time. **Figure 2.4** compares the mass, in mega-tonnes, of waste rock generated to that of the elementally rich ore produced for various elements. A closer look at this figure reveals that gold mining has the highest ratio of waste rock to the metal ore mined. This proves that massive quantities of waste rock have been generated during the gold mine activities in the country.

³⁷ Air pollution. [Accessed 08-06-2017]. Available at:
http://www.ourmineralresource.org/public_forum/55/

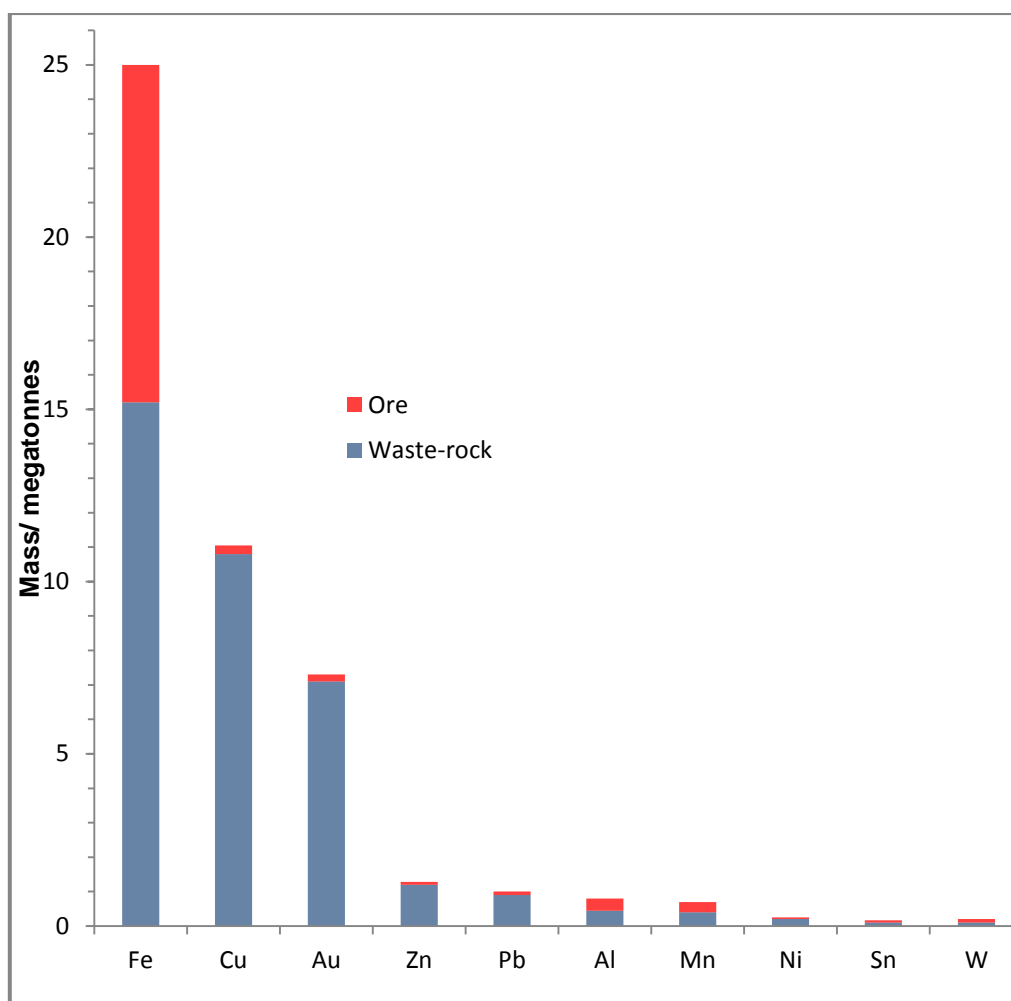


Figure 2.4: The comparison of the mass of waste rock to the ore for various elements³⁸

Tailings are the slurry that is generated as a by-product of the mineral processing activities to produce a concentrate of the element of interest and the removal of other constituents in the ore. The mineral containing the metal of interest is important to the miner, while the gangue is the remainder of the materials mined and in many cases considered as waste and therefore regarded as useless. Tailings are generated from ore which is ground into fine powder to liberate the mineral from the ore matrix and are therefore small enough to retain water.³⁹ However, toxic as tailings may be, they may also constitute a source of other valuable elements which

³⁸ Waste from consumption and production- a threat to natural resources. [Accessed 26-03-2018].

Available at: <http://www.grid.unep.ch/waste/download/waste1617.PDF>

³⁹ Tailings disposal at mines. [Accessed 06-06-2017]. Available at:

<http://technology.infomine.com/reviews/tailings/welcome.asp?view=full>

co-existed with gold in the initial ore, as well as an alternative source of gold that was lost in the initial chemical processing steps. Mine tailings are likely to contain base transition metals which include iron, copper, zinc and nickel, due to their natural occurrence in the Earth's crust as part of the ore. They may also contain valuable metals such as silver, as well as some heavy elements like arsenic and lead.⁴⁰

Water is a natural resource which is extensively used in the mining industry. The water is generally drawn from both surface and underground bodies and used at the mines for cooling down the hot underground environment (up to 65 °C), the suppression of dust during the drilling of rocks and after blasting, as well as processing of the ore and of the mineral.⁴¹ Moreover, water is used for the rinsing of the processing equipment and for vehicles used in the transportation of products. The de-watering of the underground mines has contributed to the generation of water which ends up as waste water or as a source of water where it may be used for other mining activities. Some of the water can be re-used or recycled while the rest is normally discharged into settling ponds and tailings dams.⁴² These waters which were dumped into the tailings dams (which contain different metal ions) can seep into the ground water aquifers, thus contaminating the natural underground water resources. Another process which contributes to the contamination of natural water resources is graphically presented in **Figure 2.5**. When the underground water table rises, a combination of the tailings water and ground water rises into the seepage collection ditch around the tailings dam and the mixing of the two water bodies contributes to the water contamination. The contaminated drainage water with metals which have been dissolved from the tailings can be recycled, not only in

⁴⁰ C. Falagan, B. M. Grail, D. B. Johnson. (2017). "New approaches for extracting and recovering metals from mine tailings", *Minerals engineering*, 106, pp.71-78

⁴¹ D. Stephenson. (1983). "Distribution of water in deep gold mines in South Africa", *International journal of mine water*, 2(2), pp.21-30

⁴² T. M. Askham, H. M. Van der Poll. (2017). "Water sustainability of selected mining companies in South Africa", *Sustainability*, 9(6), pp.9

order to beneficiate some valuable metals, but also to obtain cleaner water which may be used for operations at the mine site.⁴³

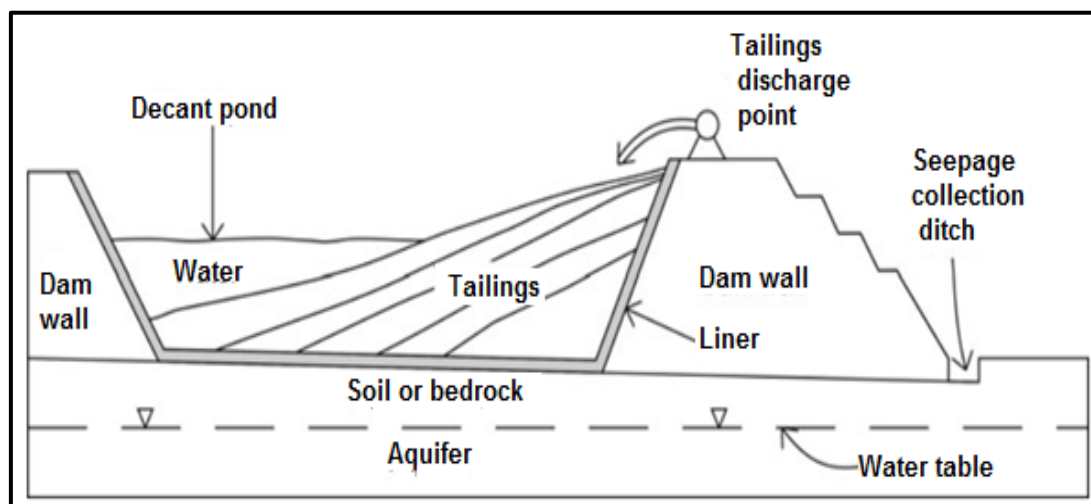


Figure 2.5: A simplified cross-section of a tailings dam.⁴⁴

A major problem encountered or caused by these contamination processes is the drastic change in pH of the water and its effect on downstream or secondary pollution and environmental damage. Research indicates that the acidity of the original tailings water is highly dependent on the processing technique that is applied⁴⁴ and indicates that processes such as leaching with thiourea produce more acidity in tailings water. Acid mine drainage (AMD) is a term used to describe the process during which acidic water is generated as a result of the chemical interaction of sulphide minerals (pyrite and pyrrhotite) with water and atmospheric oxygen and produces sulphuric acid (**Equation 2.1**).^{45,46} The potential of the formation of acid depends upon a number of physical and chemical parameters, which include the concentration of sulphide, temperature, aluminium minerals: while possible

⁴³ S. R. Rao, N. Kuyucak, T. Sheremata, M. Leroux, J. A. Finch, K. G. Wheeland. (1993). "Prospect of metal recovery/ Recycle from acid mine drainage", *Proceedings America society of mining and reclamation*, pp.223-232

⁴⁴ B. G. Lottermoser. (2010). *Mine wastes: characterization, treatment and environmental impacts*, 3rd ed., Springer, pp.208-210

⁴⁵ What is acid rock drainage. [Accessed 18-05-2017]. Available at:

<http://www.miningfacts.org/Environment/What-is-acid-rock-drainage/>

⁴⁶ K. A. Hudson-Edwards, B. Dold. (2015). "Mine Waste Characterization, Management and Remediation", *Minerals*, 5(1), pp.82-85

neutralisation of the acid with naturally occurring carbonates⁴⁶ is capable of preventing or limiting a drastic pH change. The acidity of the mine drainage which flows from the solid waste can be much higher than that from the mined mineral itself, due to the disorientated or destroyed structure of the waste compared to the natural solid structure of the rocks in the earth. The total concentration of the sulphide minerals is commonly much higher in mine tailings compared to the waste rocks and more leaching of the elements also occurs due to the smaller particle sizes of the tailings.⁴⁷ The lower water acidity also has the potential to dissolve/leach elements in the soil/waste material, specifically metal oxides and carbonates, resulting in water bodies which are rich in metal ions and may also be used as valuable elemental resources for processing.

As illustrated in **Figure 2.6**, mine water is any water which runs through the solid waste during production or as a result of natural incidents such as rain storms.⁴⁸ However, most of the acid waste water is generated from the tailings due to the fine particles of the solid materials which make the leaching of the sulphide minerals more efficient. The fine particles tend to contain higher concentrations of the different metals associated with gold-containing ore compared to the waste rocks.

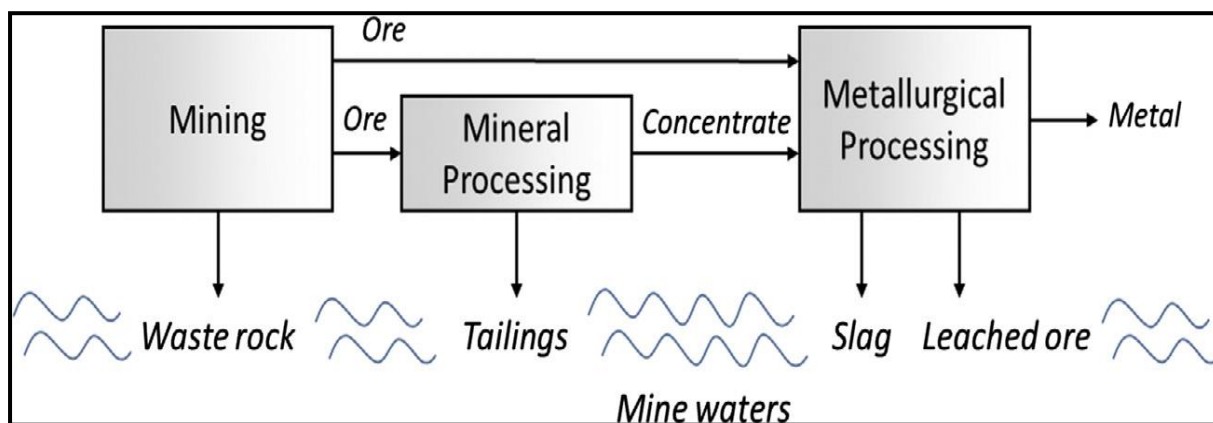


Figure 2.6: Schematic presentation of mining, mineral process and the associate waste production.⁴⁸

⁴⁷ S. H. H. Oelefse, P. J. Hobbs, J. Rascher, J. E. Cobbing, *The pollution and destruction threat of gold mining waste on the Witwatersrand - A West Rand case study*, CSIR, Natural Resources and the Environment, Pretoria, South Africa. p.2

⁴⁸ E. Lebre, G. Corder. (2015). "Integrating Industrial Ecology Thinking into the Management of Mining Waste", *Resources*, 4, pp. 765-786

2.3 THE PROCESSES OF GOLD BENEFICIATION

Several chemical processes exist, which may be successfully applied to process and isolate gold from its ore. All the processes involve a number of steps, using a wide variety of chemicals which become waste after the gold has been isolated in its pure metallic form. The four most important processes are cyanide leaching, amalgamation with mercury, leaching with alkaline sulphides or thiourea.

2.3.1 CYANIDE LEACHING

In this process, the gold is extracted predominantly from the ore matrix by leaching with an alkaline cyanide solution.⁴⁹ The finely ground ore is mixed with the sodium cyanide in the presence of activated carbon which has a high affinity for the auro-cyanide complex (**Equation 2.2**⁵⁰) and adsorbs the gold complex from the solution.⁵¹ The advantages of the cyanide leaching procedure include higher chemical stability, lower cost and a better understanding of the chemical reactions taking place as well as product isolation (the adsorption on activated carbon).⁵²



The loaded carbon may be re-used after the desorption of the gold complex by heating in the presence of sodium hydroxide (NaOH) and cyanide.^{53,54} However, this

⁴⁹ J. A. Eisele, A. H. Hunt, D. L. Lampshire. (1988). *Leaching gold-silver ores with sodium cyanide and thiourea under comparable conditions*, Report of investigations 9181, United States department of the interior

⁵⁰ Gold cyanidation. [Accessed 03-03-2018]. Available at:
https://en.wikipedia.org/wiki/Gold_cyanidation

⁵¹ R. C. Bansal, M. Goyal. (2005). Activated carbon adsorption, *Taylor & Francis group*, pp. 252

⁵² J. Zhang, S. Shen, Y. Cheng, H. Lan, X. Hu, F. Wang. (2014). "Dual lixiviant leaching process for extraction and recovery of gold from ores at room temperature", *Hydrometallurgy*, 144-145, pp.114-123

⁵³ M. J. Logsdon, K. Hagelstein, T. I. Mudder. (1999). "The management of cyanide in gold extraction", *International council on metals and the environment*, p.8

method is limited to Au which is finely distributed in a mineral matrix due to the low rate of Au dissolution/leaching and the subsequent complex formation. Other disadvantages of this Au isolation method include the interference of sulphide minerals which consume the oxygen in the reaction mixture (**Equation 2.2**), large demand for energy (costly) to liberate the gold from the refractory ores as well as the pH and temperature dependence of the leach (reaction) kinetics.⁵⁵ Cyanide may also be recovered from leach solutions using ion exchange, in which a strong base anion exchange resin may be used to absorb the metal cyanide complexes in gold waste cyanide solutions.⁵⁶

2.3.2 AMALGAMATION WITH MERCURY

Metallic gold may also be recovered from its ores by treating the ore with mercury, which readily forms an amalgam with gold and the cost of this technique is relatively low.⁵⁷ A pre-requisite for this gold recovering process is that the gold-containing ore should be finely ground (between 100 mesh and 325 mesh) to allow for the maximum exposure of the gold surface to the mercury. Water is often mixed with the ore in order to disperse the ore, thus, improving the gold-mercury interface. Additionally, most of the mercury may be recollected and re-used.⁵⁸ However, the Hg used in amalgamation as an effective solvent is not specific to gold but may also form amalgams with many other metals in the ore matrix, such as silver, arsenic, and

⁵⁴ Gold mining and processing in South Africa. [Accessed 07-03-2018]. Available at: <https://vula.uct.ac.za/access/content/group/9eafe770-4c41-4742-a414-0df36366abe6/Mining%20and%20Mineral%20Processing%20Resource%20Pack/Gold%20Learner%20Information%20sheets.pdf>

⁵⁵ Core resources. (2014). The metallurgy of cyanide gold leaching - an introduction. [Accessed 26-04-2018]. Available at:

<http://www.coreresources.com.au/the-metallurgy-of-cyanide-gold-leaching-an-introduction/>

⁵⁶ E. Goldblatt. (1959). "Recovery of cyanide from waste cyanide solutions by ion exchange", *Industrial and engineering chemistry*, 51(3), pp.241-246

⁵⁷ L. D. Lacerda, W. Salomons. (1998). Mercury from gold and silver mining: a chemical time bomb?, *Springer-Verlag Berlin Heidelberg*, p. 4

⁵⁸ Does mining use mercury?. [Accessed 17-03-2018]. Available at: <http://www.miningfacts.org/environment/does-mining-use-mercury/>

tungsten.⁵⁹ Additionally, the amalgamation with Hg usually results in the lower recovery of gold (loss of valuable income) than other methods and has the drawbacks of human exposure to the toxic mercury.⁶⁰

2.3.3 LEACHING WITH ALKALINE SULPHIDE

Another class of gold-leaching reagent is alkaline sulphide solutions. The pressure oxidation of sulphide minerals such as pyrite, chalcopyrite and arsenopyrite, which usually form part of many gold-bearing ores, results in the production of elemental sulphur or sulphate. The most important and advantageous part of this method is the accumulation of gold in the elemental sulphur, since sulphur can be readily separated from the gangue material.⁶¹ The alkaline sulphide system comprises sodium sulphide and sodium hydroxide. The lixiviation of gold is carried out in a mixture of sulphides and polysulphides. The latter are the active oxidants.⁶²

The resultant leached gold may be easily recovered by various methods, making it possible to re-use the sulphide solution. Additionally, a concentrated gold sample is produced prior to leaching and high gold recoveries may be obtained.⁶¹ The procedure may result in high S concentrations in tailings, thus giving rise to generation of AMD.

2.3.4 LEACHING WITH THIOUREA

Another popular method to process gold ore is the use of thiourea. In this process, a mixture of thiourea (H_2NCSNH_2) and dilute mineral acids is used as a lixiviant for the gold in the ore which forms a mono-cationic complex with gold (see **Equation 2.3**).

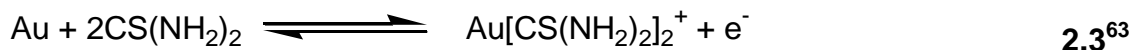
⁵⁹ J. Nicholson. (2017). "How is mercury used to purify gold", Sciencing, [Accessed 17-03-2018]. Available at: <https://sciencing.com/how-mercury-used-purify-gold-4914156.html>

⁶⁰ T. G. Chapman. (1935). Treating gold ores, 2nd ed., Arizona bureau of mines, metallurgical series no. 4, (6)3, p.10

⁶¹ M. I. Jeffrey, C. G. Anderson. (2003). "A fundamental study of the alkaline sulfide leaching of gold", *The European journal of mineral processing and environmental protection*, 3(3), pp.336-343

⁶² C. G. Anderson, L. G. Twidwell. (2008). "The alkaline sulfide hydrometallurgical separation, recovery and fixation of tin, arsenic, antimony, mercury and gold", *Lead and zinc*, The Southern African institute of mining and metallurgy, Montana, pp.121-132

The process involves the initial oxidation and conversion of thiourea into products such as formamidine disulphide ($\text{NH}_2(\text{NH})\text{CSSC}(\text{NH})\text{NH}_2$), which is more selective towards the extraction of gold.



The advantages of using thiourea instead of cyanide include lower toxicity (higher threshold limit for mammals), a higher leaching rate and less interference from base metals such as Pb, Co, Ni and Zn.⁶⁴ In addition; it is more selective towards gold and silver and requires no neutralisation step.⁶⁵ The main drawbacks of leaching with thiourea include high cost of the process and high reagent consumption.⁶⁶

2.4 THE COMPOSITION AND CHEMISTRY OF MINE WASTE

The waste from gold mines does not only comprise the naturally occurring materials which were initially mined with the gold mineral(s), but also the reagents which are used during the beneficiation processes. Despite the removal of the main or important constituents from the ore, the recovery and processing of other valuable elements from the waste may be of significant economic importance with potentially large economic and monetary value. However, before any activity can commence to attempt to recover metals from the waste, a qualitative and quantitative evaluation of the mine waste needs to be performed.

⁶³ S. Orgul, U. Atalay. (2000). "Gold extraction from Kaymaz gold ore by thiourea leaching", *Proceedings of the XXI international mineral processing congress*, Rome, Italy

⁶⁴ S. Syed. (2016). The recovery of gold from secondary sources, London, Covent garden, *Imperial college press*, p.28

⁶⁵ S. Ndlovu. (2017). Extraction of gold then, now and the future, *Building a robust mineral industry*, July 2017, Harare

⁶⁶ Thiourea gold leaching. [Accessed 01-05-2018]. Available at:
<https://www.911metallurgist.com/thiourea-gold-leaching/>

Generally, tailings are discharged in the form of slurry of about 30% solid content, highly saline and contain about 6% of pyrite by mass and a very low organic content.⁶⁷ Gold mine tailings are characterised by relatively high concentrations of transition metals, which exist mostly as silicates and may contain As, Cd, Pb, Ni, Cu, Zn, Co and Hg.⁶⁸

Literature study has indicated that uranium usually co-exists with gold in ores and as such, U may also be found in the gold processing waste. For example, the gold mine tailings in the Witwatersrand basin contain an estimate of 600 000 tons of uranium.⁶⁹ In **Figure 2.7**, the ways in which uranium can be transported from the tailings into the water in ponds surrounding the tailings dam are illustrated.

⁶⁷ Waste rock and tailings. [Accessed 11-03-2018]. Available at:
<http://www.waihigold.co.nz/mining/waste-rock-and-tailings/>

⁶⁸ M. O. Fashola, V. M. Ngole-Jeme, O. O. Babalola. (2016). "Heavy metal pollution from gold mines: environmental effects and bacterial strategies for resistance", *International journal of environmental research and public health*, 13(11), pp.1047-1066

⁶⁹ S. J. Schonfeld, F. Winde, C. Albrecht, D. Kielkowski, M. Liefferink, M. Patel, V. Sewram, L. Stoch, C. Whitaker, J. Schuz. (2014). "Health effects in populations living around the uraniferous gold mine tailings in South Africa: gaps and opportunities for research" *Cancer epidemiology*, 38, pp.628-632

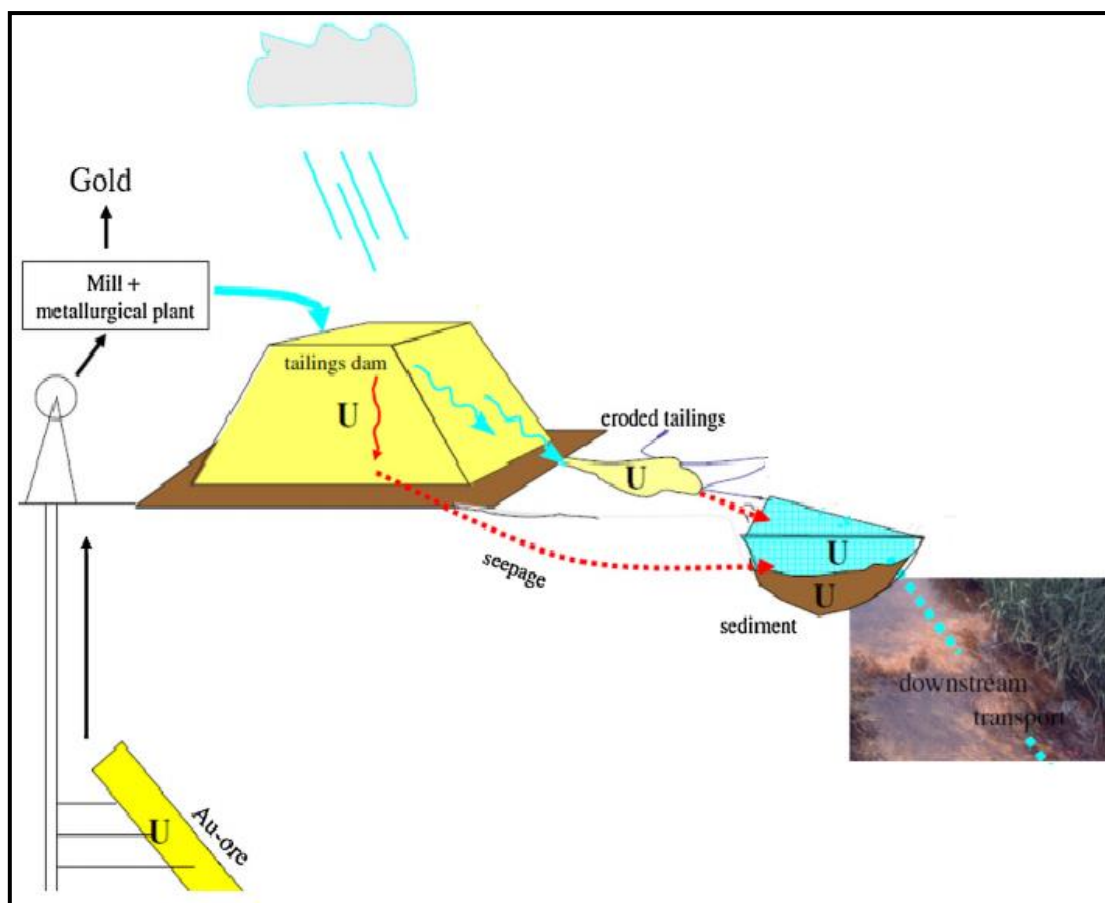


Figure 2.7: The pathways for the exposure of uranium to the surface of the earth

Cyanide, one of the processing reagents, is seldom found in tailings at high concentrations as it is usually recovered in the processing plant during the electrowinning for Au recovery before disposal of tailings. Any remaining fraction of CN^- which reaches the environment undergoes decay and becomes transformed into different chemical species (**Figure 2.7**)⁷⁰ by means of processes such as biodegradation (reaction with oxygen) and reaction with sulphur (to produce SCN^-). Additionally, a photochemical reaction facilitated by ultraviolet radiation from the sun occurs to convert cyanide into cyanate (CNO^-) which decomposes to produce ammonia (NH_3) and carbon dioxide (CO_2).

⁷⁰ Cyanide. [Accessed 03-03-2018]. Available at:

<http://www.waihigold.co.nz/mining/cyanide-ph-and-acid-drainage/cyanide/>

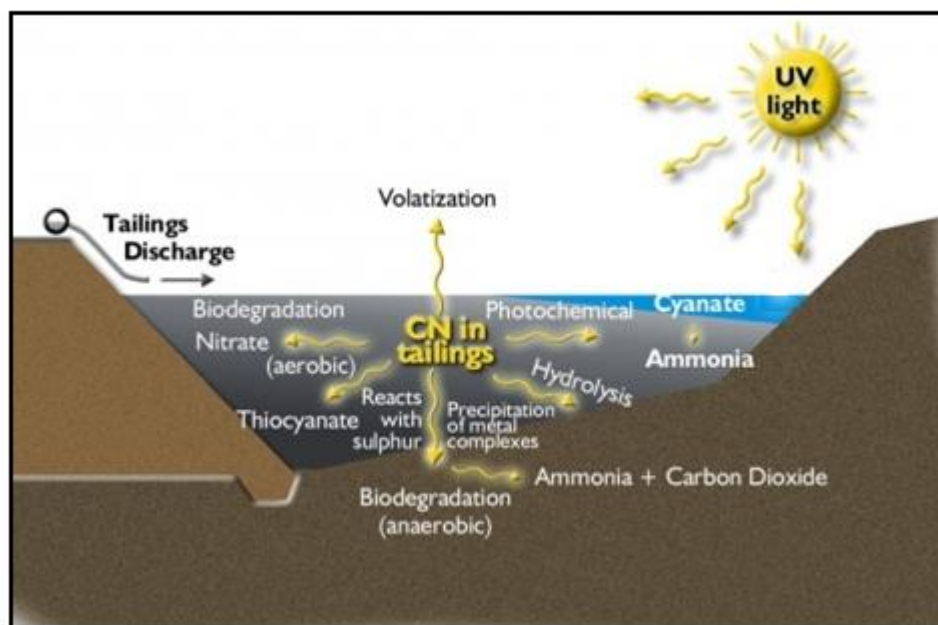


Figure 2.8: Cyanide-degradation processes in tailings dams⁷⁰

The gold mine wastes are commonly characterised by high concentrations of minerals such as pyrite, silica and quartz.⁷¹ Depending on the extraction processes and their efficiencies in gold recovery, the abundances of all the other naturally occurring elements in the waste may be very low, medium or high while elements such as Hg (**Section 2.3.2**) may be introduced as part of the beneficiation process and may exist in significant concentrations in the waste.

The acidic water formed by oxidation of sulphide minerals (mainly pyrite) may leach many metals from the solid waste, especially tailings. Therefore, the desired elements may also be found in ponds surrounding dumps of tailings and in streams as well as other water bodies surrounding the waste disposal areas.

⁷¹ T. Assawinchareonkij, C. Hauzenberger, C. Sutthirat. (2017). "Mineralogical and geochemical characteristics of tailings and waste rocks from a gold mine in northeastern Thailand". *Mine water and circular economy, Lappeenranta*, pp. 1277-1278

2.5 RE-USE AND RECYCLING OF MINE WASTE

Mine wastes are usually stored close to the mining site in different facilities, most of which are on the surface and kept exposed to the environment. From a beneficiation perspective, this is extremely convenient in that no additional mining or expensive excavation is needed to reach the source of the valuable elements. It is, however, important to utilise this waste beneficially while saving the unexplored resources and minimising its negative impact on the environment and society. While the management of waste dwells on the prevention of pollution and energy saving, treatment and disposal should be viewed as an excellent opportunity, to use it as raw material for recovery of valuable elements and to reduce the risk of pollution and negative environmental problems.

The first step in the possible beneficiation process of the different types of mine waste is a thorough evaluation of the composition of mine waste in order to determine the type and concentration of all the elements present in the waste as well as any potential harmful chemical compounds present. This is of assistance in the assessment of the profitability of recycling of the waste and is dependent on the concentrations of valuable elements in the waste. The waste may contain radioactive elements such as uranium and thorium at unacceptably high concentrations which require its removal before the normal beneficiation processes continue. It is therefore extremely important to accurately determine the qualitative and quantitative composition of mine waste prior to re-use or recycling.

Unprocessed mine waste may also be used in different applications. Waste rock, for example, may be used in asphalt paving if the properties meet the conventional requirements of paving aggregates. Tailings and waste rock may also be used in the production of wall-bricks, floor tiles, as well as the filling of earth depressions and subsidence in mined out areas and for improvement of the soil.⁷² Waste in the form of tailings and fly ash may be used to prepare inorganic porous ceramics by simply

⁷² B. G. Lottermoser. (2011). "Recycling, reuse and rehabilitation of mine wastes", *Mineralogical Society of America*, 7(6), pp.405-410

sintering the waste.⁷³ The most important use of mine waste is as a potential resource in the future for the extraction of valuable metals which they contain.

The cost of reprocessing the tailings is lower than that of processing the original ore because of the elimination of the need for mining and milling processes. The final costs or profit, however, depends on the concentration of the valuable element in the waste and the required additional costs associated with the chemical processing of the waste due to the complexity of the mineral waste (contamination due to the initial chemical processing) relative to that of the ore.⁷² It is important to note that the additional processes employed to concentrate, isolate and purify the elements in the mine waste may still not be 100% effective and the new residue or waste may still contain some of the metal of interest.⁷⁴

The potential for the reprocessing of gold mine tailings has already been recognised in South Africa. The DRD gold company, situated in Johannesburg, reported the recovery of approximately 953 kg gold (approximately 40% of their gold production) from mine tailings in the last quarter of 2013 using new technologies.⁷⁵ Mintails, another gold recycling company, located in Krugersdorp, expects to produce 58 kg of gold per month from reprocessing of approximately 350 000 tons of slimes dumps until 2025. However, not much has been reported about the evaluation and processing of mine waste in Free State and this leaves room for the potential reprocessing of these tailings for gold recovery from the mine waste distributed across the 'golden arc' from Johannesburg to Welkom. However, the important question prior to the retreatment of the mine waste in the Free State is whether the process will be economically viable or not.

⁷³ T. Liu, Y. Tang, L. Han, j. Song, Z. Lou, A. Lu. (2017). "Recycling of harmful waste lead-zinc mine tailings and fly ash for preparation of inorganic porous ceramics", *Ceramics International*, 43(6), pp.4910-4918

⁷⁴ M. Gokelma, A. Birich, S. Stopic, B. Friedrich (2016). "A review on alternative gold recovery reagents to cyanide", *Journal of Materials Science and Chemical Engineering*, 4, pp.8-17

⁷⁵ E. Nummi. (2015). From tailings to treasure? A new mother lode. [Accessed 12-03-2018]. Available at: <https://www.thermofisher.com/blog/mining/from-tailings-to-treasure-a-new-mother-lode/>

It is very important to note, moreover, that the reprocessing of the mine waste in the country is still concentrated around gold recovery, and that little or no information is available on the potential recovery of other valuable elements from these waste sites.

2.6 RECOVERY OF VALUABLE MATERIALS FROM MINE WASTE

Since minerals are non-renewable resources, it is important to ensure the maximum extraction of most of the essential commodities from the ore and to recover any valuable elements from mine waste.⁷⁶ In addition, it is of the utmost importance to treat mine waste as a valuable elemental resource and not as an environmental disaster. Waste produced in the mining industry may contain valuable elements in concentrations high enough to make their recovery profitable and reduced possible pollution and other social and economic disasters or problems.

It is important to note that not all the waste produced during mining activities may be of high economic value. The waste rock produced to render the gold ore accessible for extraction (excavation) usually contains very low concentrations of the metal of interest. Tailings, on the other hand, may contain a number of elements of interest, in significant quantities, depending on the efficiency of the beneficiation processes which were applied. Valuable elements may also be leached into water bodies and their recovery from these water bodies can be of economic and environmental importance, eliminating a dissolution step from the beneficiation process⁷⁷

A good example is the presence of uranium in the waste which is usually associated with the gold ore deposits in South Africa. Uranium which has a concentration of approximately 100 to 200 parts per million (ppm) in South African gold mine waste,

⁷⁶ J. Cui, L. Zhang. (2008). "Metallurgical recovery of metals from electronic waste: A review", *Journal of hazardous materials*, 158, pp.228-256

⁷⁷ G. Palma, J. Freer, J. Baeza. (2003). "Removal of metal ions by modified Pinus radiata bark and tannins from water solutions", *Water research*, 37(20), pp.4974-4980

may be economically removed from the gold tailings and enriched for its use in the Koeberg nuclear power station in Western Cape.⁷⁸ Possible beneficiation and isolation of the uranium may involve its leaching from the tailings with sulphuric acid.⁷⁹ It may then be recovered from the leach solution by solvent extraction and subsequent precipitation with ammonia to form ammonium diuranate.⁸⁰ Ion exchange may also be employed for tailings with low concentrations of uranium using a strong base ion exchange resin such as Amberlite (IRA-400).⁸¹

2.7 CONCLUSION

Given the above information, a great deal of research about mine waste, its potential toxicity and negative impact on society and the environment has been conducted world-wide. However, not much has been done regarding the beneficiation of other valuable elements from mine waste in the world, particularly in South Africa. Minerals are non-renewable resources and it is important to consider and explore its recycling and re-use of these resources for maximum conservation and maximum economic benefits. In addition, the large number of mines which have already closed down and the high rate of current mine closures taking place in South Africa may lead inevitably to the recycling of the waste for both the exploration of valuable metals and job creation. This cuts down on anthropogenic disasters which result from the disturbance of the orientation of underground rocks. Mining companies, world-wide, should engage in recovery of valuable materials from waste, even before disposal. The example set by mine waste reprocessing companies in Johannesburg should be

⁷⁸ P. E. Metcalf. (1996). "Management of waste from the mining and milling of uranium and thorium bearing ores", *International congress on radiation protection proceedings, South Africa*, Council for nuclear safety, South Africa, pp.391-401

⁷⁹ M. Nete, F. Koko, T. Theron, W. Purcell, J. T. Nel. (2014). "Primary beneficiation of tantalite using magnetic separation and acid leaching", *International journal of minerals, metallurgy and materials*, 21(12), pp.1153-1159

⁸⁰ J. O. Marsden, C. I. House. (2006). The chemistry of gold extraction, 2nd ed., *Society for mining, metallurgy, and exploration, Inc.*, pp.93-94

⁸¹ E. Rosenberg, G. Pinson, R. Tsosie. (2016). "Uranium remediation by ion exchange and sorption methods: a critical review", *Johnson Matthey technology review*, 60(1), pp.59-77

followed by other companies and entrepreneurs to initiate reprocessing operations in other areas, particularly the area around Welkom in the Free State province. This activity can help to minimise the volume of the waste which goes to disposal facilities and thus reduce costs associated with the disposal. Studies should also be conducted into the possible extraction of any valuable elements from the waste by the use of relatively environmentally safe and economically viable processes.

3 BENEFICIATION OF MINE WASTE: LITERATURE REVIEW

3.1 INTRODUCTION

Mine waste is an alternative source of valuable elements which may be employed in several industrial applications and day-to-day uses. Moreover, this waste is normally easily accessible for processing while no need exists for the excavation of new or virgin ore deposits. Advantages of the processing of the mine waste include conservation or remediation of the environment and the natural resources and it can also be economically viable due to lower excavation and processing costs. The same waste may pose several health issues to both humans and animals, and efforts should be made to process or re-use mine waste in order to reduce these negative impacts on society and the environment.

The recovery of different elements from samples, including from mine waste in all forms, requires a thorough qualitative and quantitative analysis of the samples in order to facilitate informed decision-making on the possible re-processing of the waste. Results of these analyses will inform the scientists on the type and quantity of the different elements present within the waste material. This in turn will determine the value of the waste (types and amounts of elements present) and the separation methods (chemistry of the elements) to be used for element beneficiation (i.e. high concentration or trace amount) and the possible impurities in the final products.

In this chapter, research conducted on the mine waste beneficiation is reviewed. The discussions in this chapter will include research on sample preparation methods such as solid dissolution, different analytical techniques and methods used for sample characterisation (qualitative and quantitative analyses) and elemental separation using ion exchange chromatography, leaching, solvent extraction and

electrowinning techniques. The outline of the general steps followed in sample preparation and analysis is illustrated in **Figure 3.1**.

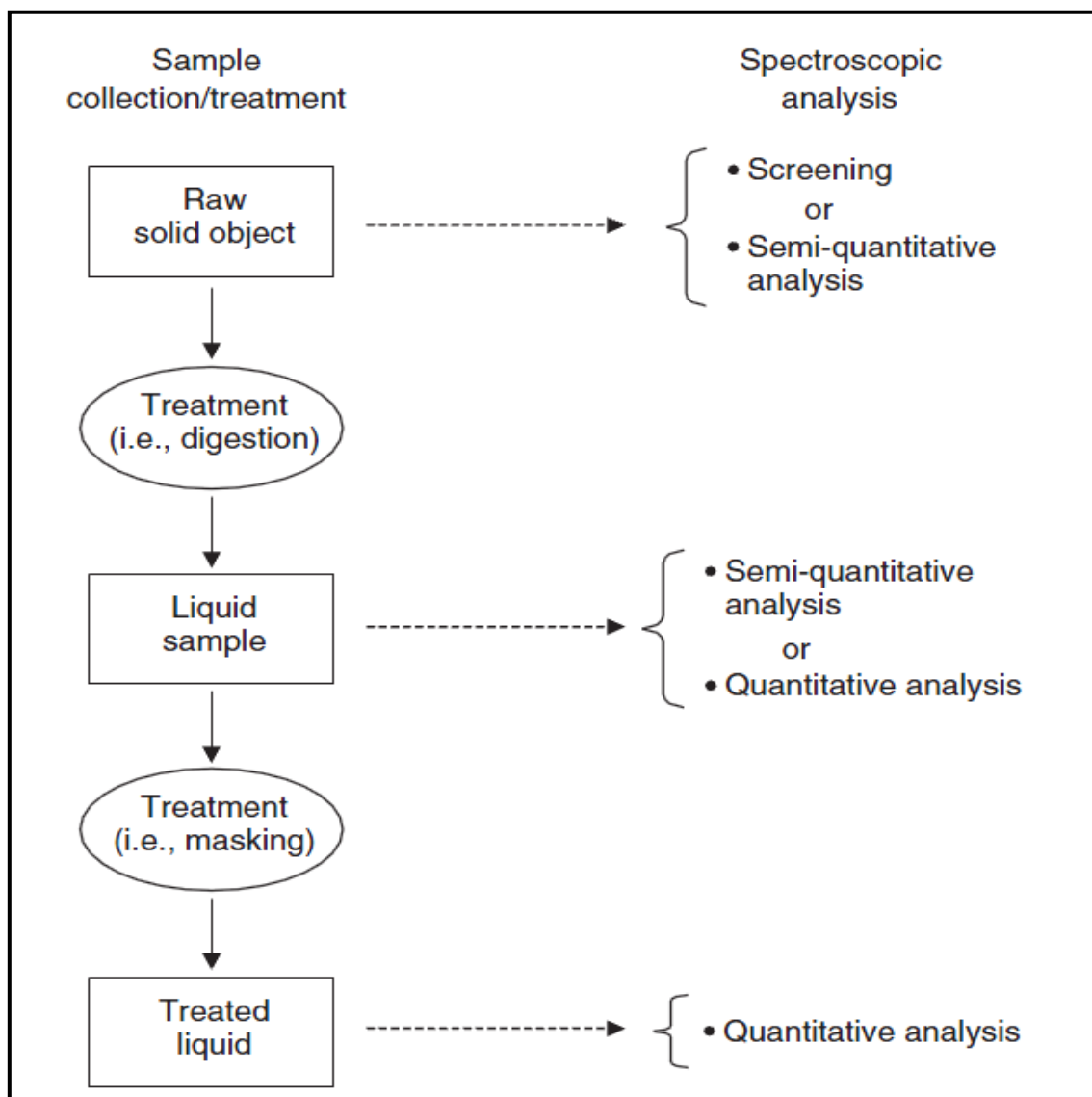


Figure 3.1: Schematic presentation of sample preparation and analysis steps⁸²

3.2 SAMPLE DISSOLUTION

A number of methods used for elemental analysis and recovery require the samples to be in liquid form, which makes sample digestion or decomposition a very

⁸² B. M. Cullum, T. Vo-Dinh. (2014). Handbook of spectroscopy, 2nd ed. Wiley VCH Verlag GmbH & Co. KGaA, p.4

important step in hydrometallurgical beneficiation processes. A literature search indicated that a number of studies have been carried out on the dissolution of rock and other solid samples. The reagents, and thus the method required for rock sample dissolution, are highly dependent on the chemical composition (type and form) of the solid samples, which include waste rock and tailings in this study. Many of the methods used for solid sample dissolution involve acid-digestion and flux fusion. The acid digestion methods included normal bench-top type dissolution (reaction of acids with basic/alkaline type of solids) or with the assistance of microwave digestion at high temperature and pressure conditions.

3.2.1 ACID DIGESTION

Hensler *et al*⁸³ report the digestion and analyses of waste samples using acid digestion. In their study, they collected a total of 21 samples on the surface of a dump as representative of the whole dumpsite. Of the 21 samples, 16 were dried at room temperature and digested with a mixture of HF, HNO₃ and HClO₄. The residue remaining after this digestion step was treated with dilute HCl prior to analysis with ICP-OES. The other 5 samples were analysed with a QEMSCAN 4300 automated mineral/phase analysis system. The ICP-OES results reported in **Table 3.1** indicated high concentrations of metals, with manganese as the most abundant among these. The QEMSCAN results showed that the waste had calcite, dolomite, smithsonite and CaSO₄ in the coarse-grained fraction, whereas the fine-grained fraction contained quartz, muscovite/illite, sphalerite, galena, pyrite and cerussite/anglesite.

⁸³ A. S. Hensler, B. G. Lottermoser, P. Vossen, L. C. Langenberg. (2016). "Automated mineral analysis to characterize metalliferous mine waste", *Earth and environmental science*, 44

Table 3.1: The average elemental composition of mine waste⁸³

| Element | Concentration (mg/L) |
|---------|----------------------|
| As | 127 |
| Cd | 397 |
| Cu | 151 |
| Mn | 3641 |
| Sb | 61 |
| Element | Percent mass (%) |
| Pb | >1 |
| Zn | >1 |

Vrkljan and Aljinovic⁸⁴ carried out a study to determine the most effective dissolution method for geochemical silicate standards called Gabbro and AGV-1. They used different mineral acid combinations in an attempt to dissolve the silicate type rock with acid combinations of HF + HNO₃, HF + H₂SO₄ and HF + HClO₄. For each mixture, a 2 g portion of the sample was wetted in a platinum dish, followed by addition of the different acid mixtures. For the HF + HNO₃ combination, 20 mL of concentrated (40%) HF was added to the 2 g sample. After digestion for 30 minutes, the reaction mixture was heated to dryness in a water bath. Another 5 mL of HF was added, followed by heating to dryness. Concentrated (65%) HNO₃ was added at intervals and evaporated to dryness. 8% HNO₃ was used for the final solution. Similar experiments were performed with the other acid combinations. The different methods were evaluated for dissolution efficiency and quantification precision with repetitions of 15 and 30 measurements. The results of this study are reported in **Table 3.2**. From these results, the researchers recommend the use of HNO₃ + HF acid combination due to the recovery of high elemental concentrations and the ease of HNO₃ evaporation.

⁸⁴ M. Vrkljan, D. Aljinovic. (2004). "Optimal method for preparation of silicate rock samples for analytical purposes", *Rud.-geol.-naft.zb*, 16, pp.59-63

Table 3.2: Trace element concentrations and variation coefficients⁸⁴

| Element | Gabbro | | | | | | AGV-1 | | | | | |
|---------|----------------------|-----------|------------------------------------|-----------|-----------------------|-----------|----------------------|-----------|------------------------------------|-----------|-----------------------|-----------|
| | HNO ₃ +HF | | H ₂ SO ₄ +HF | | HClO ₄ +HF | | HNO ₃ +HF | | H ₂ SO ₄ +HF | | HClO ₄ +HF | |
| | Conc (ppm) | CV (%) | Conc (ppm) | CV (%) | Conc (ppm) | CV (%) | Conc (ppm) | CV (%) | Conc (ppm) | CV (%) | Conc (ppm) | CV (%) |
| Co | 27 | 7 | 22 | 8 | 23 | 8 | 15 | 7 | 13 | 9 | 14 | 9 |
| Cr | 1229 | 1 | 868 | 2 | 1241 | 2 | 5 | 24 | 1 | 46 | 2 | 10 |
| Cu | 14 | 10 | 13 | 8 | 13 | 9 | 55 | 4 | 53 | 6 | 54 | 4 |
| Ni | 158 | 2 | 135 | 3 | 151 | 4 | 14 | 7 | 12 | 10 | 12 | 11 |
| Pb | 10 | 9 | 11 | 8 | 13 | 7 | 42 | 7 | 36 | 8 | 38 | 6 |
| Zn | 16 | 8 | 19 | 7 | 18 | 7 | 54 | 5 | 53 | 6 | 53 | 6 |

Conc = Concentration

CV = coefficient of variation

In another study, Totland *et al*⁸⁵ dissolved granite type samples with different acids and monitored the dissolution process using ICP-OES. Samples were weighed into polytetrafluoroethylene (PTFE) beakers and a few mL of deionised water was added to moisten the sample. 10 mL of 29 M HF and 4 mL of 12 M HClO₄ were added to the samples and the mixtures were heated on a hot plate to approximately 200 °C until a crystalline paste formed. Three more aliquots of the same acid mixture were added to the reaction mixture at intervals and the heating was repeated to incipient dryness. At this stage, HClO₄ was added and heated to get rid of HF traces by evaporation to near dryness. The residues were treated with 10 mL of 5 M HNO₃ and heated gently until clear solutions were obtained. After cooling, the solutions were transferred into 50 mL volumetric flasks and diluted with de-ionised water. The samples were further diluted by a factor of 100 and stored in polypropylene bottles. These solutions were analysed as is with ICP-OES but were further diluted by a factor of 500 before analysis with ICP-MS. The results for this study are reported in **Table 3.3**.

⁸⁵ M. Totland, I. Jarvis, K. E. Jarvis. (1992). "An assessment of dissolution techniques for the analysis of geological samples by plasma spectrometry", *Chemical geology*, 95(1-2), pp.35-62

Table 3.3: The chemical composition of granite rocks⁸⁵

| Major elements | Average percent Mass (%) | Standard deviation (%) | Reference (%) |
|--------------------------------|--------------------------|------------------------|---------------|
| SiO ₂ | - | - | 69.08 |
| TiO ₂ | 0.484 | 0.010 | 0.48 |
| Al ₂ O ₃ | 15.2 | 0.3 | 15.38 |
| Fe ₂ O ₃ | 2.55 | 0.10 | 2.66 |
| MgO | 0.802 | 0.015 | 0.75 |
| MnO | 0.0377 | 0.0009 | 0.032 |
| CaO | 2.09 | 0.05 | 1.96 |
| Trace elements | Concentration(µg/g) | | |
| Ba | 1890 | 20 | 1882 |
| Cr | 4.04 | 1.80 | 8.7 |
| Cu | 10.6 | 0.6 | 11 |
| Ni | 1.51 | 0.53 | 5 |
| Sr | 505 | 10 | 478 |
| V | 38.7 | 0.8 | 36 |
| Y | 8.50 | 0.19 | 11 |
| Zn | 90.4 | 2.1 | 86 |
| Zr | 65.1 | 1.3 | 309 |

The experimental results obtained from this study indicate that the digestion was effective as the elemental recoveries obtained were close to the expected reference values with the exception of Cr, Ni and Zr. Si was not accurately quantified due to the formation and subsequent loss of volatile SiF₄ with the addition HF. Although this may be viewed to be negative from a total chemical profiling point of view, the associated advantage is the reduction of TDS, which allows for analysis by means of ICP-MS. The values show good precision as the standard deviation values reported were very low relative to the average values, thus giving low RSDs.

Passariello *et al*⁸⁶ evaluated the environmental contamination at an abandoned mining site by the quantitative analyses of As, Cd, Hg, Pb, Sb, Sn and Zn in waste samples, ground water, surface water and air collected at this site. Solid matrices comprised 10 samples collected at different depths of the landfills and settling ponds, from ground level to a depth of 8.3 m. The mineralogical compositions of the samples were initially characterised using X-ray diffraction. These results indicated a mineralogical composition of quartz, lead, oxides and caolinite-montmorillonite, in the solid samples, with particle sizes of between 31 and 64 µm. After milling and homogenisation of the samples, about 0.1 g sample sizes were dissolved by microwave digestion in the presence of 3 mL of aqua-regia and 6 mL of 40% HF. The programme for digestion was initially 800 W for 4 minutes, repeated at 400 W for 4 minutes and finally at 800 W for 4 minutes before being cooled for 20 minutes. The results of this study are reported in **Table 3.4**.

Table 3.4: The concentrations of elements in samples taken from different depths ⁸⁶

| Depth (m) | Concentration (µg/g) | | | | | | Sb (%) |
|--------------|----------------------|------|-----|-----|------|-----|-----------|
| | As | Cd | Hg | Pb | Sn | Zn | |
| 0 - 0.3 | 2715 | 1.17 | 172 | 207 | 0.55 | 233 | 0.24 |
| 1.0 - 1.3 | 2110 | 0.88 | 120 | 215 | 0.7 | 375 | 0.25 |
| 2.0 - 2.3 | 1717 | 1.48 | 89 | 241 | 1.01 | 491 | 0.31 |
| 3.0 - 3.5 | 1634 | 0.97 | 83 | 245 | 0.98 | 497 | 0.21 |
| 4.0 - 4.5 | 1461 | 0.67 | 74 | 227 | 0.85 | 331 | 0.18 |
| 5.0 - 5.3 | 1482 | 0.79 | 70 | 226 | 0.95 | 424 | 0.23 |
| 6.0 - 6.3 | 1555 | 0.54 | 79 | 205 | 0.65 | 287 | 0.20 |
| 7.0 - 7.3 | 1544 | 0.63 | 75 | 230 | 0.88 | 393 | 0.19 |
| 8.0 - 8.3 | 2055 | 0.46 | 99 | 242 | 0.59 | 213 | 0.21 |

These results indicate that the concentration trends of the different elements vary as a function of depth. The concentration level for As decreases with an increase in

⁸⁶ B. Passariello, V. Giuliano, S. Quaresima, M. Barbaro, S. Caroli, G. Forte, G. Carelli, I. Iavicoli. (2002). "Evaluation of the environmental contamination at an abandoned mining site", *Microchemical journal*, 73(1-2), pp.245-250

depth (except for final analysis) while the concentration of lead stayed almost uniform for the samples taken at different depths. However, these results indicated some serious heavy metal contamination of the area surrounding the abandoned mine.

Mine soil samples were studied by Sahraoui and Hachicha.⁸⁷ In their study they digested 5 g portions of soil samples randomly collected in the Lakhouat mining area in Tunisia to a depth of 30 cm, using a mixture of concentrated nitric, hydrochloric and hydrofluoric acids in a volume ratio of 1:3:3 in Teflon bombs placed on a hot plate. The elemental analysis was carried out with ICP-OES. A total of 7 samples were analysed in triplicate and the concentration ranges of 692 - 2 925 ppm Pb, 2 327 - 7 629 ppm Zn and 13 - 39 ppm Cd were obtained. Rodriguez *et al*⁸⁸ digested 14 samples of mine tailings with a mixture of concentrated HNO₃ and concentrated HCl in the ratio of 3:1 (v/v) in a microwave unit. After digestion, the samples were analysed for heavy metals using ICP-OES. The results obtained indicate average concentrations of 28 453.5 mg/kg Pb, 7 000.4 mg/kg Zn, 20.6 mg/kg Cd and 308.5 mg/kg Cu. A 2711 reference standard material was used to evaluate the accuracy and the values obtained from the evaluation indicated an agreement of 83.71 - 107.70% in accuracy.

3.2.2 FLUX-FUSION

Delijska *et al*⁸⁹ investigated the different approaches to sample dissolution by flux fusion for ICP and AAS analyses. The fluxes Na₂B₄O₇, Na₂B₄O₇ + Na₂CO₃ (2:1), H₃BO₃ + KNaCO₃ + KNO₃ (10:10:1), LiBO₂ and Li₂B₄O₇ were investigated at various flux-to-sample ratios, ranging between 3:1 and 10:1. The samples were fused in Pt

⁸⁷ H. Sahraoui, M. Hachicha. (2016). "Determination of trace elements in mine soil samples using portable X-ray fluorescence spectrometer: a comparative study with ICP-OES", *KKU engineering journal*, 43(3), pp.162-165

⁸⁸ L. Rodriguez, E. Ruiz, J. Alonso-Azcarate, J. Rincon. (2009). "Heavy metal distribution and chemical speciation in tailings and solis around a Pb-Zn mine in Spain", *Journal of environmental management*, 90, pp.1106-1116

⁸⁹ A. Delijska, T. Blazheva, L. Petkova, L. Dimov. (1988). "Fusion with lithium borate as sample preparation for ICP and AAS analysis", *Fresenius Zeitschrift fir analytischechemie*, 332, pp.362-365

and graphite crucibles, and in every case, the melt was dissolved in dilute nitric or hydrochloric acids. LiBO_2 and $\text{Li}_2\text{B}_4\text{O}_7$ were found to be most effective in the fusion of silicate rocks, slag and some ores. In general, effective sample dissolution was observed for the relatively low flux to the sample ratio (3:1) while the 10:1 ratio with $\text{Li}_2\text{B}_4\text{O}_7$ as flux proved to be better for samples containing high concentrations of metals and sulphur. In this study, reference samples were prepared and analysed to evaluate the accuracy of the method. Evaluation of the results indicated that samples were effectively dissolved and quantified with precision (relative standard deviation) that varied between 0.5 and 1.0%.

Cantillo *et al*⁹⁰ decomposed estuarine sediments by fusion with lithium metaborate and monitored the decomposition with direct plasma emission spectrometry. About 1.0 g of lithium metaborate was weighed in a graphite crucible followed by the addition of 0.2 g portions of the sample in a small depression made in the flux. The mixture was heated for 15 minutes in a muffle furnace at 950 °C and the liquid borate bead was transferred into a Teflon FEP beaker containing 100 mL of 5% HNO_3 . The content was stirred for 10 minutes using a magnetic stirrer and the resulting solution was transferred into 125 mL polyethene bottle. Working standards were prepared by the dilution of the stock standard solution with 5% HNO_3 and the analysis was performed.

The concentrations and mass percentages of elements in the NBS estuarine sediment (SRM-1646) are presented in **Table 3.5** as determined by two different analysts. The precision of the method was evaluated with a replicate analysis of six samples and the coefficients of variation were found to be less than 10% for all the elements with the exception of Co, Zn and Dy.

⁹⁰ A. Y. Cantillo, S. A. Sinex, G. R. Helz. (1984). "Elemental analysis of estuarine sediments by lithium metaborate fusion and direct current plasma emission spectroscopy", *Analytical chemistry*, 56(33), pp.33-37

Table 3.5: The elemental composition of the NBS estuarine sediment (SRM-1646)⁹⁰

| Element | Analyst 1 (n = 6) | Analyst 2 (n = 6) |
|---------|----------------------|-------------------|
| | Percent mass (%) | |
| Al | 5.3(2) | 5.4(1) |
| Si | 30(3) | 30(1) |
| Ti | 0.36(2) | 0.37(2) |
| Fe | 2.9(2) | 3.0(0) |
| Element | Concentration (µg/g) | |
| V | 89(3) | 91(3) |
| Cr | 74.1(1) | 70(4) |
| Mn | 280(2) | 280(2) |
| Co | 17(18) | 20(14) |
| Ni | 31(5) | 37(6) |
| Cu | 28(9) | 28(6) |
| Zn | 130(0) | 120(13) |
| Ga | 19(8) | 19(6) |
| Y | 17(8) | 15(4) |
| Zr | 270(4) | 300(4) |
| La | 36(2) | 36(3) |
| Ce | 110(4) | 110(7) |
| Dy | 2.8(7) | 3.1(14) |
| Yb | 2.2(4) | 2.0(5) |

() = coefficient of variance

Wittmann and Willay⁹¹ developed a new sample preparation method using a flux comprising 15% boric acid and 85% lithium metaborate in an automatic device called PLASMASOL that transforms powdered samples into liquids in a composite crucible. The crucible is composed of an external container made up of a platinum alloy and the interior being of glassy carbon. Certified reference materials were used in this study to evaluate the performance of the PLASMASOL that included certified low grade Lorraine iron ore and electric furnace dust samples.

⁹¹ A. A. Wittmann, G. M. H. Willay. (1985). "Automatic non-metallic sample preparation for inductively coupled plasma spectrometry", *Spectrochimica Acta*, 40B(1/2), pp.253-261

0.250 g portions of the samples were mixed with 1.500 g of the flux mixtures in the composite crucible and heated for 4 minutes at 1100 °C. The final solutions were diluted to 500 mL with deionised water and analysed with ICP-OES. The results of this study are reported in **Table 3.6**. The new method returned elemental recoveries very close to those of the certified mass percentage values. The measurements were repeated 10 times to evaluate the precision and repeatability of the method and the standard deviation values of the analysed samples were found to be lower than the certified values.

Table 3.6: The reference and measured mass percentages⁹¹

| Element | Lorraine iron ore/ % (CRM) | | | | Electric furnace dust | | | |
|---------|----------------------------|-------|------------|-------|-----------------------|-------|------------|--------|
| | CRM | | ICP (n=10) | | CRM | | ICP (n=10) | |
| | Mean | SD | Mean | SD | Mean | SD | Mean | SD |
| Fe | 24.2 | 0.08 | 23.9 | 0.30 | 24.85 | 0.17 | 24.7 | 0.35 |
| Si | 3.4 | 0.04 | 3.43 | 0.06 | 1.71 | 0.04 | 1.80 | 0.043 |
| Ca | 18.0 | 0.14 | 17.85 | 0.17 | 3.43 | 0.13 | 3.25 | 0.055 |
| Al | 1.99 | 0.05 | 1.94 | 0.018 | 0.33 | 0.026 | 0.15 | 0.006 |
| Ti | 0.106 | 0.005 | 0.101 | 0.001 | 0.047 | 0.004 | 0.044 | 0.0008 |
| Mg | 0.69 | 0.14 | 0.79 | 0.008 | 1.31 | 0.03 | 1.26 | 0.018 |
| P | 0.55 | 0.018 | 0.59 | 0.013 | 0.128 | 0.007 | 0.131 | 0.008 |
| Mn | 0.295 | 0.015 | 0.289 | 0.006 | 2.84 | 0.04 | 2.86 | 0.02 |

In another study, lithium metaborate proved to work well in the decomposition of silicate rocks. Van Loon and Parissis⁹² decomposed twelve standard silicate rocks of different composition with LiBO₂ flux fusion using a sample-to-flux ratio of 1:7 and dissolving the melt with dilute HNO₃. In their study, they mixed the sample with the flux in a porcelain crucible and transferred to a pre-ignited graphite crucible for 15 minutes at 900 °C. Satisfactory results were obtained and the percent oxide masses for the different elements did not deviate significantly from those reported by other researchers.

⁹² J. C. Van Loon, C. M. Parissis. (1969). "Scheme of silicate analysis based on the lithium metaborate fusion followed by atomic-absorption spectrophotometry", *The analyst*, 94(1125), pp.1057-1062

A modified method for the dissolution and analysis of tungsten in mine samples was developed by Storms *et al*⁹³. In the altered method, they fused the sample with LiBO₂ in a graphite crucible at 1000 °C for 15 minutes, using a sample-to-flux ratio of 1:2. The melt was transferred to a water-containing Teflon beaker and heated to dryness, followed by addition of 5 mL of HF. The mixture was then evaporated to dryness and perchloric acid was added. After evaporating to dryness, HCl was used to leach the residue. 5 mL of the clear solution was transferred to a borosilicate test-tube, 5 mL of stannous chloride was added and the solution was heated in a water bath at 85 °C for 10 minutes. The test-tube was removed from the water bath and 3 mL of dithiol solution was added with gentle swirling. The solution was allowed to cool to room temperature and 5 mL of petroleum spirit was added, followed by vigorous shaking for 30 seconds. Absorption measurements were carried out at 630 nm. A certified reference material, Canmet TLG-1, with a certified W concentration of 830 ppm was analysed in 25 replicates and the concentration was found to be 846 ± 12 ppm. A similar analysis was performed on mica-schist and a leucogranite and indicated 219 ± 6 ppm and 17 ± 1 ppm respectively.

3.3 ELEMENTAL QUANTIFICATION USING SPECTROSCOPIC TECHNIQUES

3.3.1 UV/VISIBLE SPECTROSCOPY

Kumari *et al*⁹⁴ studied the elemental content in mine and surface water near the Sukinda chromite mining area in Odisha, India in order to compare the dissolved chemical content present in the two different water bodies. Water samples were collected from nine different mine sites while surface water samples were collected

⁹³ L. Storms, A. Bonne, W. Viaene. (1980). "The use of lithium metaborate fusion for the spectrophotometric determination of tungsten in silicate rocks using zinc dithiol", *Journal of geochemical exploration*, 13, pp.51-56

⁹⁴ B. Kumari, R. K. Tiwary, K. K. Srivastava. (2017). "Physico-chemical analysis and correlation study of water resources of the sukinda chromite mining area, Odisha, India", *Mine water and the environment*, 36(3), pp.356-362

from ten locations in the Damsal Nala and the Brahmani River. Temperature and pH measurements were carried out at the site with digital pH meter and thermometers. The dissolved oxygen (DO) was analysed immediately after sampling while other parameters such as total hardness (TH), total dissolved solids (TDS), alkalinity, chloride and sulphate contents were determined by means of standard laboratory methods. The TH was determined with EDTA-titrations and Eriochrome black T as indicator, while Cr (VI) was determined by spectrophotometry with 1,5-diphenylcarbazide in an acidic medium. The results of the two types of samples are reported in **Table 3.7** as the ranges of parameters.

Table 3.7: Parameter ranges of surface water and mine water⁹⁴

| Parameter | Mine water | Surface water |
|------------------------------|--|---------------------------|
| Temperature (°C) | 23.9 - 25.9 | 27.5 - 30.0 |
| pH | 7.2 - 8.4 | 6.6 - 7.7 |
| DO | - | 4.7 - 7.5 |
| TH (mg/L) | 62 - 245 | All within WHO* standards |
| TDS (mg/L) | 165 - 344 | |
| Alkalinity (mg/L) | 60 - 325 | 50.6 - 78.2 |
| Cl- concentration (mg/L) | 9.70 - 21.09 | 13.3 - 48.0 |
| Sulphate concentration(mg/L) | 23.45 - 113.1 | 9.8 - 50.4 |
| Cr (VI) concentration(mg/L) | ⁱⁿ 0.33 - 0.98 → ^e 0.02 - 0.30 | 0.02 - 0.23 |
| Cr concentration | ⁱⁿ 0.46 - 1.26 → ^e 0.03 - 0.91 | 0.041 |

*TH max. limit = 300 mg/L. TDS max. limit = 1000 mg/L.

ⁱⁿ- influent concentration, ^e- effluent concentration.

The results in **Table 3.7** indicate significantly higher concentrations of the elements in mine water than in surface water-bodies, with the exception of the chloride ion. The cause of the difference could be the contamination of water by the waste products generated by the mine. The treatment of mine water decreased the concentration of Cr but the removal was not effective as the concentrations after treatment remained higher than those in surface water.

3.3.2 PLASMA SPECTROSCOPY

Inductively coupled plasma optical emission spectroscopy (ICP-OES) and inductively coupled plasma mass spectrometry (ICP-MS) have been used extensively for the elemental analysis of geological samples that include rocks and minerals as well as ores.⁹⁵ These techniques have also been applied world-wide in the determination of the chemical composition of primary and secondary wastes produced in the mining industry. In most cases, the motivation originated from environmental concerns in order to find ways to make the waste less harmful. Very few studies were conducted, based on the beneficiation possibilities, particularly in South Africa. The kinds of waste that were analysed include waste rock dumps, tailings and water in ditches as well as AMD flowing in streams.

3.3.2.1 Inductively coupled plasma optical emission spectroscopy (ICP-OES)

Zhou *et al*⁹⁶ investigated the distribution of antimony and arsenic in water-bodies around or near the Xikuangshan (XKS) mine in China. A total of 34 water samples were collected from XKS in polyethylene bottles, comprising 4 surface water samples, 1 mine water sample, 1 leaching water sample and 28 ground water samples from springs connected to different aquifers. The samples were then filtered and acidified with HNO₃. The cations were analysed by ICP-OES and detection limits of 0.01 mg/L were obtained. The maximum concentrations of Sb and As were contained by water collected from areas that receive ground water from waste dumpsites and tailings ponds. The highest Sb concentration was 39.2 mg/L and As had the highest concentration of 1.8 mg/L. The overall mean concentrations of Sb and As were found to be 3.74 mg/L and 0.19 mg/L respectively.

⁹⁵ M. Totland, I. Jarvis, K. E. Jarvis. (1992). "An assessment of dissolution techniques for the analysis of geological samples by plasma spectrometry", *Chemical geology*, 95, pp.35-62

⁹⁶ J. Zhou, T. M. Nyirenda, L. Xie Y. Li, B. Zhou, Y. Zhu, H. Liu. (2017). "Mine waste acidic potential and distribution of antimony and arsenic in waters of the Xikuangshan mine, China", *Applied Geochemistry*, 77, pp.52-61

Paula *et al*⁹⁷ determined the concentrations of arsenic, which is associated with gold ores, in mine tailings using ICP-OES. The samples were digested using an open ultrasonic bath and a microwave oven. A standard arsenic solution of concentration 1000 mgL⁻¹ was used for calibration and reference solutions. 2 M hydrochloric acid and sodium borohydride tablets (1.5% in 0.2% NaOH) were used for hydride-generation. HNO₃, HCl and H₃PO₄ were diluted with ultra-pure water to prepare the solutions for analyses. The mine samples were sonicated for an hour, centrifuged and the supernatants were transferred to 15 mL polyethene tubes for arsenic quantification while for microwave-assisted acid digestion, duplicate portions of the mine tailings were transferred into Teflon tubes. A mixture of HNO₃ and HF (3:1) was added and these samples were digested for 15 minutes and then heated to 200 °C and digested for another 15 minutes at this temperature. H₃BO₃ was added, after cooling the solution to room temperature, to neutralise the excess HF before the heating programme was repeated. The samples were cooled, diluted, stored at 5 °C and later analysed. The microwave-digested samples gave a concentration of 1 385.0 ± 41.0 mg/kg As with acceptable precision (RSD= 2.96%).

Ko *et al*⁹⁸ studied the contamination of soils and sediments by mine activities close to the Myungbong gold mine in Korea. Samples of mine tailings, sediments, soils and water were collected from the area. Solid samples were digested in aqua-regia, and then analysed for As, Cu, Cd and Pb by ICP-OES. The concentration of As in the tailings was found to be in the range of 2500 - 6420 mg/kg, whereas the concentrations of the other elements were comparatively low. The paddy and farmland soils collected downward from the dumps of tailings contained average As concentrations of 92 mg/kg and 129 mg/kg respectively. Water samples from different bodies were also analysed and the pond, stream, domestic well 1 and domestic well 2 had As concentrations of 140, 27, 2.0 and 28 µg/L respectively.

⁹⁷ J. F. R. Paula, R. E. S. Froes-Silva, V. S.T. Ciminelli. (2012). "Arsenic determination in complex mining residues by ICP OES after ultrasonic extraction", *Microchemical journal*, 104, pp.12-16

⁹⁸ I. Ko, J. S. Ahn, Y. S. Park, K. Kim. (2003). "Arsenic contamination of soils and sediments from tailings in the vicinity of Myungbong Au mine, Korea", *Chemical speciation and bioavailability*, 15(3), pp.67-74

In a different approach, Yaghmaeian *et al*⁹⁹ removed inorganic mercury from an aqueous solution by the use of multi-walled carbon nanotubes. A solution of mercury was prepared with HgCl₂ and de-ionised water. 100 mL aliquots of Hg solutions of concentrations 0.1, 1 and 10 mg/L were placed in 250 mL batch reactors. Dilute solutions (1 M) of HNO₃ and NaOH were used for pH control. The solutions were then shaken at the rate of 150 rpm at 25 °C in an incubator shaker and then filtered to separate the solution from adsorbents. The filtrates were acidified to a pH < 2 with HNO₃. The solutions were stored at 4 °C in glass containers and a cold vapour ICP-OES system was used to analyse for mercury. The effects of different variables were investigated and it was found that the rate of adsorption is directly proportional to pH and the extent of removal increases with pH in the range 3 - 7. The contact time of 120 minutes was deemed the best. The initial concentration was found to be inversely proportional to the initial amount of mercury as concentrations of 0.1 mg/L, 1 mg/L and 10 mg/L yielded removal percentages of 71.4%, 63.6% and 45.6% respectively.

Servida *et al*¹⁰⁰ investigated the compositions of the waste rock dumps at Rosia Montana gold mine in Alba. Twenty-five composite samples were collected, of which each was divided into two portions for mineralogical and geochemical analyses. The samples were sieved into different particle sizes from 10 mm to less than 0.063 mm in order to investigate the relationship between the particle size and the chemical processes. The fraction of size less than 2 mm was ground to a fine powder in an agate jar. XRF was used to analyse the samples for major elements, S and trace elements which include Ba, Zr, Rb, Sr, V and Y using powder disc samples. The concentrations of the potentially toxic elements (PTE) namely Ag, As, Cu, Ni, Pb and Zn, were determined by ICP-OES on solutions prepared by the microwave digestion of the solid samples in an aqua-regia medium. Arsenic was analysed by the hydride method. Triplicate analyses were performed on all the different elements and the

⁹⁹ K. Yaghmaeian, R. K. Mashizi, S. Nasser, A. H. Mahvi, M. Alimohammadi, S. Nazmara. (2015). "Removal of inorganic mercury from aquatic environments by multi-walled carbon nanotubes", *Journal of environmental health science and engineering*, 13(55), pp.1-9

¹⁰⁰ D. Servida, S. Comero, M. D. Santo, L. Capitani, G. Grieco, P. Marescitti, S. Porro, F. L. Forray, A. Gal, A. Szakacs. (2013). "Waste rock dump investigation at Rosia Montana gold mine (Romania): a geostatistical approach", *Environmental Earth Sciences*, 70(1), pp.13-31

coefficients of variance were below 10%. The samples were divided into two groups, WR1 and WR2 whereby WR1 comprised SiO₂ content of range 56.58 - 63.80%, whereas WR2 had the range of 50.04 - 52.88%. The results showed concentrations of elements as presented in **Table 3.8**

Table 3.8: Concentrations of PTEs in samples¹⁰⁰

| Sample label | Concentration (mg/kg) | | | | |
|--------------|-----------------------|-------|------|------|-------|
| | Ag | As | Cu | Ni | Pb |
| WR1 | 4.3 | 117.5 | 30.4 | 3.4 | 42.5 |
| WR2 | 1.7 | 47.3 | 9.0 | 29.7 | 108.1 |

3.3.2.2 Inductively coupled plasma mass spectrometry (ICP-MS)

Shinotsuka and Ebihara¹⁰¹ developed a method for the quantification of REEs, Th and U in chondritic meteorites using ICP-MS. A stock REE standard solution was prepared by dissolving pre-ignited REE oxide of 99.9% purity and 1000 mg/L U and Th commercial standard solutions. The stock solution was used to prepare standard solutions by dilution. For the ICP-MS analysis, 10 mg of the sample was transferred into a Teflon beaker, followed by addition of 0.21 mL of HF, 0.15 mL of HNO₃ and 0.09 mL of HClO₄. The mixture was heated at 150 °C for 24 hours while the beaker was covered with a screw cap. The sample was then heated to dryness in an evaporation chamber. The residue was dissolved in 1.2 mL of 7 M HNO₃ and diluted to 10 mL with water. The solution was then divided into 2 portions. The smaller portion of 1 mL was diluted again to 10 g to determine Y. A mixed internal standard was then added to the sample solutions as well as to the reagent blank and standard solutions. For RNAA, three mixed standard solutions were prepared from the same stock solutions as those used for the ICP-MS analysis. The 10 REEs namely La, Ce, Nd, Sm, Eu, Gd, Tb, Tm, Yb and Lu were analysed by radiochemical neutron activation analysis (RNAA). The results are presented in **Table 3.9**.

¹⁰¹ K. Shinotsuka, M. Ebihara. (1997). "Precise determination of rare earth elements, thorium and uranium in chondritic meteorites by inductively coupled plasma mass spectrometry- a comparative study with radiochemical neutron activation analysis", *Analytical ChimicaActa*, 338(3), pp.237-246

The analyses were carried out in duplicate for RNAA while the reported ICP-MS results are the mean values of four analyses and excellent reproducibility were obtained. Both the ICP-MS and RNAA results show good consistency between the two methods.

Table 3.9: Analytical results for the meteorite using ICP-MS and RNAA¹⁰¹

| Element | RNAA | | | | ICP-MS | |
|---------|----------------------|-------|------|-----------|----------------------|-----------|
| | Concentration (ng/g) | | | | Mean | |
| | Run 1 | Run 2 | Mean | Error (%) | Concentration (ng/g) | Error (%) |
| Y | - | - | - | - | 2412 | 1.8 |
| La | 647 | 521 | 584 | 1.7 | 503 | 1.9 |
| Ce | 1420 | 1290 | 1360 | 0.66 | 1260 | 1.2 |
| Pr | | - | - | - | 197 | 1.8 |
| Nd | 993 | 1070 | 1030 | 4.4 | 977 | 0.57 |
| Sm | 319 | 325 | 322 | 0.49 | 318 | 2.2 |
| Eu | 113 | 107 | 110 | 0.36 | 108 | 2.9 |
| Gd | 427 | 420 | 424 | 2.9 | 394 | 1.6 |
| Tb | 65.2 | 74.6 | 70.0 | 0.98 | 69.0 | 1.5 |
| Dy | - | - | - | - | 466 | 2.5 |
| Ho | - | - | - | - | 95.4 | 3.9 |
| Er | - | - | - | - | 288 | 5.0 |
| Tm | 51.2 | 54.1 | 52.7 | 2.3 | 49.6 | 3.2 |
| Yb | 308 | 356 | 322 | 0.59 | 311 | 2.2 |
| Lu | 50.8 | 54.2 | 52.5 | 0.57 | 45.6 | 9.7 |
| Th | - | - | - | - | 61.0 | 4.8 |
| U | - | - | - | - | 15.4 | 2.2 |

- = Information not provided

Zhou *et al*¹⁰² studied the soil contamination in the vicinity of the Dabaoshan Mine in the Guangdong Province of China. ICP-MS was used to analyse the soil for the total element concentrations and focused on the potentially toxic or heavy metals which include Cu, Zn, Cd and Pb. Forty-eight samples of tailings, and paddy, garden and control soils were collected from areas close to Dabaoshan Mine. The surface soils were taken to a depth of 20 cm and stored in PVC bags prior to air-drying for 7 days at room temperature. The samples were then finely ground and sieved through a 150-mesh stainless-steel screen. Smaller portions of the samples were then digested with a mixture of the acids HNO₃, HClO₄ and HF and analysed with ICP-MS for total of heavy metal content. The results indicated that Cu, Zn, Cd and Pb concentrations were significantly higher in the tailings than in the other soils, followed by paddy soil, garden soil and the control soil. The tailings had concentrations of 1486, 2516, 6.42 and 429 mg/kg for Cu, Zn, Cd and Pb respectively.

3.3.3 ATOMIC ABSORPTION SPECTROSCOPY (AAS)

Kryazhov *et al*¹⁰³ proposed a method for the quantitative determination of gold, lead, nickel and cobalt in a mineral using AAS equipped with a graphite furnace and suggested that the same method can be applied to ores, rocks and waste in the mining industry. Acid digestion was employed together with flux fusion for decomposition of the sample. A set of AAS VARIAN AA 240 DUO equipment was used and included a flame VARIAN 240F and electro-thermal VARIAN 240AZ spectrometers. Graphite cuvette VARIAN was used as the electro-thermal atomiser with ultra-pure nitrogen as the purge gas. Gold was extracted and its solution was concentrated while other metals were analysed without prior concentration. The method was controlled with Au and Pb reference materials which gave an accuracy of below 28% for Au, 30% for Pb, Ni and Co. The analysed elements have proved to have high interference in this method.

¹⁰² J. M. Zhou, Z. Dang, M. F. Cai, C. Q. Liu. (2007). "Soil heavy metal pollution around the dabaoshan mine, Guangdong Province, China", *Pedosphere*, 17(5), pp.588–594

¹⁰³ A. Kryazhov, S. Panova, N. Kolpakova, A. Pshenichkin. (2014). "Determination of Au, Pb, Ni and Co in mineral raw materials by atomic absorption spectroscopy with graphite furnace", *Procedia chemistry*, 10, pp.437-440

Yann *et al*¹⁰⁴ evaluated the amount of arsenic and other elements released into the Xichu River from mine wastes at La Aurora mine, in Mexico. Samples were collected with clean polyethene containers which were rinsed with the same sample. They were then filtered by the use of 0.22 µm Millipore membranes and acidified with concentrated nitric acid. Parameters such as pH, temperature, electric conductivity, dissolved oxygen, alkalinity and sulphide concentration were measured at the source. The elemental content was determined in the laboratory in the laboratory using AAS. **Table 3.10** reports only the percentages of the elements which exceed the maximum permissible levels (MPL) according to the Mexican norm.

Table 3.10: Percentages of analysed samples that exceeds the MPL for drinkable water in Mexico¹⁰⁴

| Parameter | MPL (mg/L) | % over MPL (n = 47) |
|-----------------|------------|---------------------|
| As | 0.025 | 34.0 |
| Cd | 0.005 | 8.5 |
| Cu | 2.0 | 12.8 |
| Fe | 0.3 | 23.4 |
| Mn | 0.2 | 93.6 |
| SO ₄ | 400.0 | 48.9 |
| Zn | 5.0 | 12.8 |

Moreno *et al*¹⁰⁵ developed a method for the analysis of total mercury content in liquid matrices of mine tailings. A Spectrosol atomic absorption solution of mercury nitrate was used as the primary standard. Liquid samples containing Hg were added to the Hg vapour-generation flask, followed by 10 mL of 0.5 M hydrochloric acid. Sodium borohydride was used as a reducing agent to generate elemental Hg in a solution of 5% NaBH₄ and 1% potassium hydroxide (w/v). Triplicate samples of tailings (1 g) were weighed into 50 mL polypropylene pots, followed by the addition of 15 mL of

¹⁰⁴ R. A. Yann, G. A. Armando, C. R. Irene, G. V. Moises, M. A. Raul. (2017). "Arsenic liberation from mine wastes derived of skarn deposits at Sierra Madre oriental, Mexico", *Procedia earth and planetary science*, 17, pp.833-836

¹⁰⁵ F. N. Moreno, C. Anderson, R. Stewart, B. Robinson. (2009). "Analysis of mercury-rich plants and mine tailings using the hydride-generation AAS method", *Brazilian archives of biology and technology*, 52(4), pp.953-960

aqua-regia. The digestion of samples was carried out in water-baths at 80 °C and the filtrates were diluted with water purified with reverse osmosis. Results obtained from this study reported mercury values with very low LOD (11.4 ng/mL) and good reproducibility (RSD = 4.6%, n =10). Extraction of Hg with (NH₄)₂S₂O₃ was also carried out and compared to the aqua-regia extraction method. The method in which 2 g/L (NH₄)₂S₂O₃ solution was used resulted in relatively higher Hg recoveries (122.2 ± 9.4 mg/Kg) compared to those of the aqua-regia method (67.47 ± 11.2 mg/Kg).

Hsu *et al*¹⁰⁶ investigated the removal of arsenate from acid mine drainage through catalytic oxidation in the presence of Fe ions and neutral aluminium atoms. Zero-valent aluminium (ZVAI) samples were prepared by cutting Al metal into small square pieces of side 5.0 mm long. Aluminium beverage cans (AIBC) were collected and their samples were prepared by removing coating from the surface, using a steel brush and cutting them into pieces of similar dimensions to those of the ZVAI pieces. AIBC and ZVAI of surface area 0.0068 and 0.0028 m²g⁻¹ were used in a single batch of the As(III) oxidation. A stock solution of 20 mM As(III) was prepared and 1 mL of this solution was transferred into a 250 mL glass vessel sealed with a cap and equipped with two Teflon tubes to allow the inflow and outflow of air. The pH of the solution was adjusted to 1 and the concentration changed to 80 µM. The solution was then purged with air for 10 minutes, followed by addition of 1 g of ZVAI, while maintaining the purging with air to keep the dissolved oxygen levels at 8 ± 0.7 mg/L. The solution was extracted in intervals of time and the concentration of As(III) was determined using AAS. Results indicated that 80 µM As was completely removed in the AIBC system at a pH of 6 and As(III) was converted to As(V).

Lin¹⁰⁷ studied the chemical properties of leachates and precipitates formed in a sulphide ore waste rock dump of the Rudolfsgruvan nickel mine in Central Sweden. The dump was divided into the leached and accumulation horizons. In Pit 3, a 220

¹⁰⁶ L. C. Hsu, K. Y. Chen, Y. T. Chan, Y. Deng, C. E. Hwang, Y. T. Liu, S. L. Wang, W. H. Kuan, Y. M. Tzou. (2016). "Catalytic oxidation and removal of arsenate in the presence of Fe ions and zero-valent Al metals", *Journal of hazardous materials*, 5(317), pp.237-245

¹⁰⁷ Z. Lin. (1996). "Leachate Chemistry and precipitates mineralogy of Rudolfsgruvan mine waste rock dump in Central Sweden", *Water Science and Technology*, 33(1), pp.163-171

cm excavated profile, three samples (L1-L3) from the leached horizon and 5 samples (A1 - A5) from the accumulation horizon were collected. Crushed rock samples were transferred to polyethylene flasks containing 100 mL de-ionised water and thoroughly mixed in a rotating shaker for 8 days in order to produce leachates for chemical analysis. The samples were then filtered and divided into 2 portions. The first was immediately analysed for pH, Eh, Al, SiO₂ and SO₄²⁻. The other portion was acidified with HNO₃ and analysed for K and Na by atomic emission spectroscopy while atomic absorption spectroscopy was used to analyse for Ca, Cu, Cd, Fe, Mg, Ni, Pb and Zn. The results are reported in **Table 3.11**.

Table 3.11: The pH and concentrations of chemical species in leachates of waste rock samples¹⁰⁷

| Sample label | pH | Concentration (mg/L) | | | | | | | | | | | | |
|--------------|------|----------------------|----|-----|------|----|-----|-----|----|----|----|----|------------------|-------------------------------|
| | | Cu | Zn | Cd | Fe | Al | Pb | Ni | Mg | K | Na | Ca | SiO ₂ | SO ₄ ²⁻ |
| L1 | 2.90 | 18.5 | 11 | - | 150 | 10 | 8.2 | 11 | 2 | 6 | 3 | 7 | 110 | 1440 |
| L2 | 3.21 | 8.3 | 92 | - | 330 | 9 | 3.1 | 98 | 59 | 15 | 7 | 5 | 118 | 1560 |
| L3 | 3.59 | 6.0 | 46 | 2.8 | 680 | 4 | 3.5 | 270 | 17 | 5 | 3 | 3 | 38 | 3264 |
| A1 | 3.60 | 0.7 | 46 | 2.9 | 740 | 3 | 3.5 | 290 | 17 | 3 | 1 | 2 | 39 | 3360 |
| A2 | 3.90 | 0.3 | 48 | 2.9 | 1080 | 3 | 3.6 | 280 | 14 | 4 | 1 | 2 | 38 | 3840 |
| A3 | 3.96 | 0.3 | 63 | 3.8 | 1010 | 3 | 4.5 | 310 | 18 | 4 | 4 | 2 | 41 | 3600 |
| A4 | 3.92 | 0.5 | 51 | 3.2 | 720 | 2 | 3.6 | 300 | 16 | 5 | 2 | 2 | 36 | 3360 |
| A5 | 3.85 | 0.6 | 56 | 3.5 | 830 | 2 | 3.7 | 320 | 18 | 5 | 3 | 2 | 25 | 3600 |

3.3.4 SCANNING ELECTRON MICROSCOPY AND ENERGY DISPERSIVE X-RAY SPECTROSCOPY (SEM-EDS)

The main advantage of this technique is that the chemical analysis is conducted on solid samples and no sample dissolution is needed, while its major drawback is its inability to accurately quantify elements in micro- and ultra-micro range. However, this technique provides very useful information on the type of the elements present in unknown samples while it gives a very good estimate of the quantity of the major elements present. With a roughly known chemical composition, the digestion becomes less difficult as quite precise methods may be employed, followed by a very accurate wet analysis.

Romero *et al*¹⁰⁸ conducted a detailed geochemical study at a dormant mine in Santa Lucia, in western Cuba by analysis of waste samples at the mine site. A total of 21 waste rock samples were collected in and around the Santa Lucia mine site. The samples were crushed, quartered, pulverised in an agate mortar to 200 mesh, and homogenised. The chemical composition of the samples was determined by analysis with SEM-EDS and this revealed, amongst others, the presence of Pb, S, Fe and As.

Rieuwerts *et al*¹⁰⁹ determined the mineralogical composition of potentially arsenic-containing mine waste and stream sediments in a historic metal mining area in England, in the United Kingdom. Mine waste samples were collected from 13 distinct spoil dump sites at 5 abandoned mines in the Tamar catchment, namely at Devon Great Consols (4 samples, DGC1-4), Gawton (2 samples, GW1-2), New Great Consols (2 samples NGC1-2), Gunnislake Clitters (3 samples, GC1-3) and Okeltor (2 samples, OK 1-2). Five sub-samples were also taken at each site, at the centre and at each corner of a square metre grid at depths between 2 and 5 cm. The samples were crushed using a mortar and pestle, and then prepared and analysed by means of SEM-EDS. The results (**Table 3.12**) revealed that the samples were dominated by quartz and other silicates. The samples also contained iron oxides, carbonates and jarosite.

¹⁰⁸ F. M. Romero, R. M. Prol-Ledesma, C. Canet, L. N. Alvares, R. Perez-Vazquez. (2010). "Acid drainage at the inactive Santa Lucia mine, western Cuba: Natural attenuation of arsenic, barium and lead, and geochemical behavior of rare earth elements", *Applied geochemistry*, 25, pp.716-727

¹⁰⁹ J. S. Rieuwerts, K. Mighanetara, C. B. Braungardt, G. K. Rollinson, D. Pirrie, F. Azizi. (2014). "Geochemistry and mineralogy of arsenic in mine wastes and stream sediments in a historic metal mining area in the UK", *Science of the total environment*, 472, pp.226-234

Table 3.12: The mass percent mineral composition of rocks from waste dumps in England¹⁰⁹

| Mineral | Percent mass mineral content (%) | | | | | | | | | | |
|------------------------------------|----------------------------------|------|------|------|------|------|------|------|------|------|------|
| | DGC | | NGC | | GW | | GCM | | OKT | | Mean |
| | 1 | 2 | 1 | 2 | 1 | 2 | 1 | 2 | 1 | 2 | |
| Quartz | 46.0 | 25.7 | 54.0 | 14.0 | 46.1 | 31.4 | 45.7 | 19.4 | 36.3 | 25.9 | 34.4 |
| Other silicates | 28.7 | 32.7 | 43.1 | 17.9 | 28.5 | 12.1 | 50.0 | 64.3 | 18.4 | 14.4 | 31.0 |
| Fe-O _x /CO ₃ | 11.9 | 27.1 | 0.5 | 2.8 | 5.0 | 4.3 | 2.2 | 11.0 | 19.9 | 8.7 | 9.3 |
| Jarosite | 0.1 | 4.4 | 0.1 | <0.1 | 1.4 | 1.5 | 0.1 | 1.7 | 2.2 | 0.4 | 1.2 |
| Scorodite | 4.5 | 4.1 | 1.4 | 63.8 | 15.1 | 22.2 | 0.1 | 0.6 | 17.7 | 48.2 | 17.8 |
| Arsenopyrite | 1.7 | 0.2 | <0.1 | 0.4 | 1.3 | 5.0 | <0.1 | 0.1 | 1.5 | 0.5 | 1.1 |
| Other As forms | 0.1 | 0.2 | <0.1 | 0.1 | 1.5 | 19.6 | <0.1 | 0.1 | 0.8 | 0.8 | 2.3 |
| Other minerals | 6.9 | 5.6 | 0.9 | 1.2 | 1.1 | 3.9 | 1.9 | 2.9 | 3.2 | 1.2 | 2.9 |

3.3.5 GAMMA RAY SPECTROSCOPY

Darko *et al*¹¹⁰ measured the amounts of naturally occurring radioactive materials (NORMS) in mine tailings, ore, soil, water and air samples from two open-pit mines in Ghana, especially the uranium-thorium series. The analyses were carried out by gamma spectroscopy and radon concentration measurements, using solid-state nuclear track detectors. The samples were dried in air for a week in the laboratory and for 48 hours in an oven at 50 °C. They were then finely ground and allowed to stand for 3 - 4 weeks and their radioactivity was measured/counted for 50 000 s.

¹¹⁰ O. E. Darko, A. Faanu, R. A. Awudu, G. Emi-Reynolds, J. Yeboah, C. O. Oppon, H. E. Akaho. (2010). "Public exposure to hazards associated with natural radioactivity in open-pit mining in Ghana", *Radiation protection dosimetry*, 138(1), pp.45-51

Table 3.13: Average absorbed and annual effective dose rates from external gamma rays in the two mines and their surroundings¹¹⁰

| Mine | Location | Absorbed dose rate (nGy h) | | Mean annual effective dose ($\mu\text{Sv a}^{-1}$) |
|------|-------------------|----------------------------|-------------------------|--|
| | | Range | Mean | |
| 1 | Processing plants | 40 - 140 | 58.5 ± 16.7 | 71.7 ± 20.5 |
| | Tailing dams | 50 - 120 | 63.4 ± 17.3 | 77.8 ± 19.7 |
| | Ore stockpiles | 40 - 130 | 68.0 ± 21.0 | 83.9 ± 26.0 |
| | Estates/suburbs | 51 - 98 | 55.7 ± 68.3 13.7 | 68.3 ± 13.7 |
| | Villages | 40 - 120 | 57.8 ± 6.4 | 70.9 ± 19.2 |
| 2 | Processing plants | 40 - 50 | 49.8 ± 5.8 | 61.0 ± 7.3 |
| | Tailing dams | 53 - 127 | 76.7 ± 11.8 | 94.8 ± 13.5 |
| | Ore stockpiles | 50 - 80 | 78.0 ± 5.6 | 95.7 ± 6.9 |
| | Estates/suburbs | 50 - 80 | 68.6 ± 11.8 | 86.6 ± 5.0 |
| | Villages | 45 - 110 | 75.8 ± 12.4 | 93.0 ± 15.2 |

The results in **Table 3.13** indicate no significant difference of the calculated doses between the two mines. The mean annual effective dose for the two mines was determined as 0.3 ± 0.06 mSv. This value falls within the accepted value of less than 1 mSv y^{-1} according to the ICRP for public exposure control.

Faanu *et al*¹¹¹ assessed the natural and anthropogenic radioactivity levels in rocks, water and soils within and around the operation area of the Chirano Gold Mine in Ghana by gamma spectrometry. A total of 50 samples was randomly collected from selected points in the mine and surroundings. Of the 50 samples, 28 were soil, rock and ore samples, whereas the other 22 were water samples. The solid samples were

¹¹¹ A. Faanu, H. Lawluvi, D. O. Kpeglo, E. O. Darko, G. Emi-Reynolds, A. R. Awudu, O. K. Adukpo, C. Kansaana, I. D. Ali, B. Agyeman, L. Agyeman, R. K. Kpodzro. (2014). "Assessment of natural and anthropogenic radioactivity levels in soils, rocks and water in the vicinity of Chirano gold mine in Ghana", *Radiation protection dosimetry*, 158(1), pp.87-99

air-dried on trays in the laboratory for 7 days and oven-dried at 105 °C for 3 to 4 hours. The dry samples were then finely ground with a ball mill and sieved through a 2 mm mesh into beakers. The Marinelli beakers were completely sealed for a month to allow the short-lived daughters of ^{238}U and ^{232}Th decay series to equilibrate with their long-lived parent radio-nuclides. The water samples were homogenised and transferred into a 1 L Marinelli beaker, weighed, sealed and stored for a month. The radioactivity counts were measured, using a high-purity germanium detector (HPGE). The measured dose rates varied per sample in the range 20 – 230 nGyh⁻¹, giving a mean value of 71.0 ± 18.0 nGyh⁻¹ and thus a mean annual effective dose of 87 ± 22 µSv in the range 44 – 142 µSv. The value is higher than the global average absorbed dose rate measured from terrestrial gamma radiation in outdoor air, reported by United Nations Scientific Committee (UNSCEAR), of 59 nGyh⁻¹.

Ongori *et al*¹¹² used gamma radiation measurements to determine the radon releasing rate from a tailing dumpsite at a non-operational mine dump at the Kloof mine, near Westonaria in Gauteng, South Africa. Thirty-four soil samples were collected from the mine dump at a depth of between 30 and 50 cm at five locations at the dumpsite. The samples were dried overnight at 105 °C and the moisture content was determined. The dry grains were then crushed with a mortar and pestle and sieved through a 1 mm mesh. The dry samples were stored in Marinelli beakers for at least 21 days to equilibrate the gamma-emitters ^{226}Ra , ^{214}Bi and ^{214}Pb in the uranium series and ^{228}Ac , ^{208}Tl and ^{212}Pb in the thorium decay series. A low-background Hyper Pure Germanium γ -ray detector system was used to analyse the dry soil samples. The mean activity concentrations in the soil samples were 308 ± 7 Bqkg⁻¹, 255 ± 5 Bqkg⁻¹ and 18 ± 1 Bqkg⁻¹ for ^{238}U , ^{40}K and ^{232}Th respectively. The mean normalised radon flux for the mine dump was found to be 0.12 ± 0.02 Bqm⁻²s⁻¹.

¹¹² N. J. Ongori, R. Lindsay, T. R. Newman, P. P. Maleka. (2015). "Determining the radon exhalation rate from a gold mine tailings dump by measuring the gamma radiation", *Journal of environmental radioactivity*, 140, pp.16-24

3.4 RECOVERY OF ELEMENTS BY ADSORPTION

Adsorption is considered a very cost-effective method for elemental recovery or removal as the materials used in this technique are normally quite inexpensive. The technique is used to recover metal ions in solution. Various physical conditions influence the rate and degree of adhesion of different metals to the material. These conditions are controlled or altered to separate the various ions in the solutions selectively. The method has been used successfully to recover metals from AMD selectively, with high percent recoveries.

Geremias *et al*¹¹³ studied the removal of acidity, Al(III), Fe(III) and Mn(II) from acid mine drainage, using coal mining waste. AMD samples were collected from mines in the carboniferous region of Criciúma, Brazil. The coal mine waste was calcined at 800 °C for 1 hour in a muffle furnace and characterised by XRD after determination of surface area. The metal oxide content in the waste was determined by AAS prior to adsorption experiments. Coal acid mine drainage (AMD) samples were collected from underground sources and their pH was determined, using a pH meter while the concentrations of Al(III), Fe(III) and Mn(II) were determined by AAS. Treatment of AMD with waste in a batch system was carried out by placing 50 mL of the AMD with different masses of the waste and stirring at 200 rpm at room temperature to the equilibrium point of the pH. To treat the AMD in a continuous flow system, the samples of the AMD were passed through a column packed with 13 g of the waste and the flow rate was kept constant (1 mL/min) using a peristaltic pump. The pH was monitored throughout the process while 10 mL aliquots were periodically collected and analysed for elemental content. Results obtained from this study indicated that the batch system needed about 2.0 g of waste to raise the pH from the original 2.6 to 7.8 after 48 hours. The elemental quantification results indicated a 100% removal of

¹¹³ R. Geremias, R. Laus, J. M. Macan, R. C. Pedrosa, M. C. M. Laranjeira, J.

Silvano, F. V. Fávere. (2008). "Use of coal mining waste for the removal of acidity and metal ions Al(III), Fe (III) and Mn (II) in acid mine drainage", *Environmental Technology*, 29(8), pp.863-869

Al(III) and Fe(III) while 89% Mn(II) was removed at the same time. In the case of the continuous flow system, the pH immediately rose from 2.6 to 12.5. However, with a volume of 300 mL AMD, the pH increased to only 4.8, suggesting that acid and metal ion removal was more efficient in a batch system.

Oyewo *et al*¹¹⁴ studied the efficiency of banana peels as an effective adsorbent in waste water treatment. Fresh wet banana peels were cut into small pieces, washed with de-ionised water and sun-dried for 10 days. The dried peels were then crushed finely in a planetary continuous ball mill machine at 200 rpm, using powder to ball ratio of 10:1 and screened to get a particle size of less than 65 µm. Different batches of the banana peel material was then treated with HNO₃ and NaOH respectively. Mine tailing seepage was collected from a gold mine situated 40 km south-west of the Gauteng province in South Africa. The study investigated the possible adsorptive capability of banana peels as nanosorbent material in the removal of radioactive materials from aqueous mine waste water bodies. The mine water collected at this site had 55.8 mg/L and 18.8 mg/L of U and Th respectively. Water samples were stirred at 200 rpm for 24 hours in the presence of the banana peel material and then filtered, using syringe filter of pore size 0.45 µm. The filtrate was analysed for U and Th with an ICP-OES. Very interesting results were obtained, which indicated the removal of 99.9% of the Th and 70% of the U at pH 3.0.

Aktas and Morcali¹¹⁵ recovered platinum from a platinum-containing waste solution by adsorption by the use of activated carbon. The waste sample was collected from a PGM treatment plant in Istanbul, Turkey, containing 57.6 mg/L Pt at pH of 3.5. Serial experiments were carried out to test the effects of different factors. The first set of experiments were carried out by varying the amount of activated carbon; in the second set, the stirring rate was varied from 40 to 200 r/min while in the third set, the stirring time was varied between 1 and 5 hours. The highest adsorption percentage of Pt was observed when 400 mg activated carbon was used after shaking for 3

¹¹⁴ O. A. Oyewo, M. S. Onyango, C. Wolkersdorfer. (2016). "Application of banana peel nanosorbent for the removal of radioactive minerals from real mine water", *Journal of Environmental Radioactivity*. 164, pp.369-376

¹¹⁵ S. Aktas, M. H. Morcali. (2011). "Platinum recovery from dilute platinum solutions using activated carbon", *Transitions of nonferrous metals society of China*, 21, pp.2554-2558

hours at the rate of 200 r/min and a temperature of 70 °C which removed more than 99.9% of the Pt from the original solution. At room temperature, the extent of Pt adsorption dropped to 77%. Further investigation revealed that activated carbon has a capacity of 2.7 mg per gram of platinum.

Ayala and Fernandez¹¹⁶ investigated the feasibility of the removal of heavy metals from mine waste leachate using spent coffee grounds. The spent coffee grounds were collected from a cafeteria in northern Spain. Some of the coffee grounds were washed (WCG) while others were used unwashed (UCG). Both types were air-dried and stored in sealed polyethylene bottles. A synthetic solution was prepared by the dilution of a stock solution containing 1000 mg/L of cadmium, nickel and zinc which were prepared with their respective sulphate salts. A series of polyethylene bottles containing coffee waste (10 g/L) and solutions of metals were shaken at 75 rpm at room temperature, followed by filtration. The pH of the filtrate was measured, followed by analysis by AAS. Different batch experiments were carried out to investigate the effects of contact time, pH, initial concentration of metal, amount of adsorbent and the effect of other metal ions in the matrix. It was observed that the degree of heavy metal removal rose with increasing amount of adsorbent as the recoveries improved significantly when the dosage of adsorbent was augmented. The degree of removal also increased along with the contact time, as well as did the pH in the range between 2 and 7.

3.5 PRECIPITATION

Feng *et al*¹¹⁷ characterised AMD from a South African gold mine and treated it with lime and sulphide as possible precipitants. Lime was added to the AMD sample up to a pH of 12.5 but quantification indicated incomplete precipitation. In another attempt, a sample of AMD was treated with H₂O₂ and the pH was raised to 5. This was

¹¹⁶ J. Ayala, B. Fernandez. (2018). "Treatment of mining waste leachate by the adsorption process using spent coffee grounds", *Environmental technology*

¹¹⁷ D. Feng, C. Aldrich, H. Tan. (2000). "Treatment of acid mine water by use of heavy metal precipitation and ion exchange", *Minerals engineering*, 13(6), pp.623-642

followed by addition of sodium sulphide (Na_2S) and subsequent addition of lime in order to adjust the pH to 8. The results in **Table 3.14** indicate that most of the metal ions were removed by over 99% in these conditions

Table 3.14: The concentrations of metal ions before and after precipitation with lime and sodium sulphide¹¹⁷

| | Species | After oxidation | Lime + Na_2S precipitation | | |
|----------------------|------------------|-----------------|--|----------------------------|----------------------------|
| | | | 0.6x Na_2S | 0.8x Na_2S | 1.0x Na_2S |
| pH | | 1.45 | 8.0 | 8.0 | 8.0 |
| Concentrations (ppm) | Cr^{2+} | 4.85 | 0.0001 | 0.0001 | 0.0001 |
| | Cu^{2+} | 1.80 | 0.0020 | 0.0018 | 0.0015 |
| | Fe | 942 | 0.2142 | 0.2142 | 0.2141 |
| | Mn | 112 | 0.0899 | 0.0873 | 0.0789 |
| | Ni^{2+} | 5.75 | 0.0441 | 0.0364 | 0.0342 |
| | Pb^{2+} | 0.349 | 0.0015 | 0.0011 | 0.0010 |
| | Ti^{2+} | 3.549 | 0.005 | 0.0049 | 0.0048 |
| | Zn^{2+} | 10.1 | 0.0001 | 0.0001 | 0.0001 |
| | Zr^{2+} | 0.0919 | 0.0500 | 0.0498 | 0.0495 |
| | Cd^{2+} | 0.260 | 0.0018 | 0.0013 | 0.0009 |
| | Co^{2+} | 1.94 | 0.005 | 0.0048 | 0.0042 |

X = the theoretical amount of Na_2S that is required to react with all the ions in solution

Matlock *et al*¹¹⁸ developed a method to precipitate heavy metals from acid mine drainage samples that were collected from an abandoned mine in Kentucky, USA. A sodium salt of benzenediamidoethanethiol (BDET) ligand was synthesised from isophthaloyl dichloride, 2-mercaptoethylamine hydrochloride and triethylamine. Previously analysed 500 mL aliquots of the raw AMD samples were stirred and BDET was added at a molar ratio of 1:1 to the total dissolved metals. The solutions were stirred for 20 hours, 10 mL aliquots were collected in time intervals, filtered, acidified and analysed by ICP-OES. The results indicated very promising elemental

¹¹⁸ M. M. Matlock, B. S. Howerton, D. A. Atwood. (2002). "Chemical precipitation of heavy metals from acid mine drainage", *Water research*, 36, pp. 4757 - 4764

recovery via precipitation and 99.995% iron and 97.269% manganese were removed from the mine drainage solution. This method significantly reduced the amount of metal waste formed during well-known treatment methods while it also minimised the amount of base to be added for neutralisation of the acid.

Blue *et al*¹¹⁹ developed a method to precipitate mercury from aqueous solutions with the use of 1,3-benzenediamidoethanethiol (BDTH₂), which was specifically synthesised for this investigation. An aqueous solution of HgCl₂ was mixed with an excess amount of BDTH₂ in ethanol. A white precipitate that formed immediately was filtered and air-dried. The BDT-Hg precipitate was characterised by infrared spectroscopy and had a melting point of 156 °C. The analyses of Hg were carried out using cold vapour atomic absorption spectrometer. In addition to the 100% yield, this method proved to be more time-effective in Hg recovery or removal.

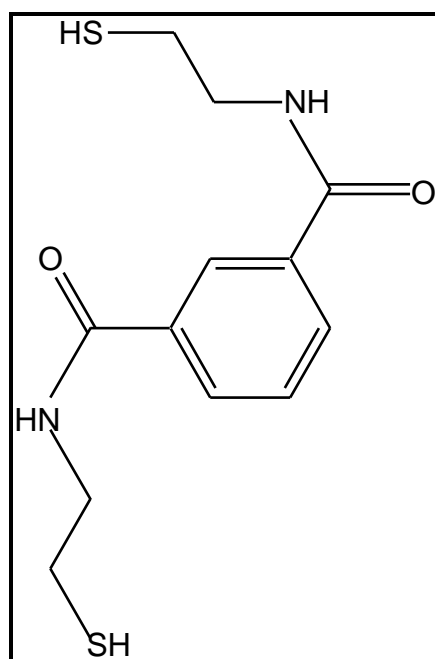


Figure 3.2: The structure of BDTH₂¹²⁰

¹¹⁹ L. Y. Blue, P. Jana, D. A. Atwood. (2010). "Aqueous mercury precipitation with the synthetic dithiolate, BDTH₂", *Fuel*, 89, pp.1326-1330

¹²⁰ Chemspider. [Accessed 08-04-2018]. Available at:
www.chemspider.com/Chemical-structure.19238563.html

Chen *et al*¹²¹ investigated the recovery of Fe, Cu, Zn and Mn from AMD. Sludge samples were collected from the Liwu mud-retaining dam (LWMRD) in China with Fe, Cu, Zn and Mn content of 45.91%, 11.58%, 31.06% and 7.95% respectively. The water samples were filtered to remove suspended solids and stored at 4 °C in polyethylene bottles. Fe²⁺ ions were oxidised with 30% H₂O₂ addition followed by a four step precipitation process with the addition of Ca(OH)₂ and Na₂S solutions. This method removed 99.51%, 86.09%, 87.87% and 79.71% Fe, Cu, Zn and Mn from the main water and decreased the metal concentrations in the effluent to levels below the limits set by federal regulations.

In another study, Santos *et al*¹²² investigated the selective removal of iron from AMD by precipitation/bio-sorption. This study was carried out in an attempt to improve on the traditional hydroxide precipitation method that proved to be non-selective. The elemental content in the AMD was determined and a synthetic mixture of similar composition was prepared, using the metal sulphate salts of the metals. The concentrations were then accurately determined by atomic absorption spectroscopy while that of ferrous iron was determined by titration with potassium dichromate. Two different biomasses prepared from grape stalks and cork powder were suspended in the synthetic solution and stirred for a specific contact time. A cationic polyelectrolyte, Zetag 64, was added up to a concentration of 10 mg/L to induce flocculation while stirring for further 20 seconds. The solid was allowed to settle and the supernatant was analysed for metals. Results indicated the removal of 98% Fe, 82% Cu and 40% Zn and Ni at pH 4 while at pH 3, 65% Fe was removed, with only 5% Cu.

Wei *et al*¹²³ investigated the selective removal of iron and aluminium from AMD by employing a two-step precipitation process. AMD samples were collected at the entrance to the treatment channel and stored in polyethene bottles at 4 °C. Fe²⁺ was

¹²¹ T. Chen, B. Yan, C. Lei, X. Xiao. (2014). "Pollution control and metal resource recovery for acid mine drainage", *Hydrometallurgy*, 147(148), pp.112-119

¹²² S. Santos, R. Machado, M. J. N. Correia, J. R. Carvalho. (2004). "Treatment of acid mining waters", *Minerals engineering*, 17, pp.225-232

¹²³ X. Wei, R. C. Viadero Jr, K. M. Buzby. (2005). "Recovery of iron and aluminium from acid mine drainage by selective precipitation", *Environmental engineering science*, 22(6), pp.745-755

completely oxidised to Fe^{3+} with compressed air and the solutions were filtered. Fe was recovered by controlling the pH with the addition of 10 N NaOH in an effort to determine the recovery of Fe at different pH values. The remaining filtrate used as the feedstock for the Al recovery which was also carried out by addition of NaOH to pH values ranging between 4.5 and 8.0. The efficiencies of other bases such as Na_2CO_3 , NH_4OH , CaO and $\text{Ca}(\text{OH})_2$ were investigated in this study. More than 98.6% iron with a purity greater than 93.4% was recovered in the pH range of 3.5 – 4.0. Aluminium was recovered at a rate of 75% in the pH range 3.5 – 4.5 while almost total recovery was obtained in the 5.0 – 8.0 pH range. **Table 3.15** summarises the recoveries of the two metals using the different bases that were used to control the pH.

Table 3.15: The performances of metal recovery using different reagents¹²³

| Reagent | Fe precipitation | | Al precipitation | |
|--------------------------|------------------|------------|------------------|------------|
| | Recovery (%) | Purity (%) | Recovery (%) | Purity (%) |
| NaOH | 98.6 | 97.5 | 97.2 | 94.7 |
| Na_2CO_3 | 98.6 | 97.7 | 97.2 | 95.0 |
| NH_4OH | 99.0 | 94.2 | 97.2 | 94.5 |
| CaO | 99.2 | 96.6 | 97.2 | 94.1 |
| $\text{Ca}(\text{OH})_2$ | 99.2 | 96.4 | 97.2 | 72.2 |

Tolonen *et al*¹²⁴ investigated the removal of sulphate from mine water by precipitating it as ettringite ($\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12} \cdot 26\text{H}_2\text{O}$), as well as the use of the precipitate as a sorbent to remove arsenate. The effluent water from the underground mine drainage (pH \approx 7.9) was treated with ferric sulphate at the mine site and then sampled after at the settling pond and 800 mL sample was transferred into a 1 L glass beaker at room temperature. Hydrated lime and sodium aluminates were then added to the mine water sample. 0 - 2 ppm, of an experiment-dependent polymer was added to the sample, followed by the mixing of the solution for 5 hours at 50 rpm, using a programmable paddle stirrer after which the solution was left to

¹²⁴ E. T. Tolonen, T. Hu, J. Ramo, U. Lassi. (2016), "The removal of sulphate from mine water by precipitation as ettringite and the utilization of the precipitate as a sorbent for arsenate removal", *Journal of Environmental Management*, 181, pp.856-862

allow the mixture to settle. After an hour and overnight settling, water samples were taken for sulphate, nitrate, calcium, sodium and aluminium analyses. Nitrate and sulphate analyses were carried out with ion exchange chromatography while calcium, sodium, aluminium and arsenic were analysed with ICP-OES. The treatment of mine water removed 85 - 90% sulphate from the original 1400 mg/L. The aluminium and sodium concentrations increased during the treatment but remained below 11 mg/L and 285 mg/L respectively. The concentration of calcium remained constant at 312 mg/L in most cases. A moderate decrease in the nitrate concentration was observed during treatment.

3.6 RECOVERY OF METALS BY LEACHING

Xie *et al*¹²⁵ carried out leaching experiments to determine the optimal conditions for the recovery of Ni, Cu and Co from low-grade Ni-Cu sulphide tailings. The metal composition of the tailings was determined by a standard analytical method and found to be 0.24%, 0.25%, 0.01%, 10.25% in Ni, Cu, Co and Fe content respectively. A 20 g portion of dry tailings was soaked in distilled water in an evaporating dish. Known volumes of nitric and sulphuric acids were added while stirring. The slurry was then leached with distilled water, in a beaker, while stirring vigorously for 30 minutes at room temperature and atmospheric pressure. The suspension was then centrifuged and the residue was washed with three portions of distilled water, filtered and combined with the leaching mixture. The total leaching mixture was filtered and the volume was measured. Further investigations were carried out by varying the H₂SO₄ and HNO₃ volumes added, with a fixed total acidity. The temperature was fixed at 100 °C while the time was fixed at 2 hours. Results indicated that both Ni and Co leaching varied directly with the amount of HNO₃, while Cu followed the same trend up to a certain point, whereas Fe leaching decreased at lower H₂SO₄ additions.

¹²⁵ Y. Xie, Y. Xu, L. Yan, R. Yang. (2005). "Recovery of nickel, copper and cobalt from low-grade Ni-Cu sulfide tailings", *Hydrometallurgy*, 80, pp.54-58

Jiang *et al*¹²⁶ recovered valuable metals from a zinc leaching residue (ZLR) by sulphate roasting and water leaching. The residue was a by-product of the traditional zinc hydrometallurgical process, which contained large amounts of heavy metals which included zinc, lead, manganese, cadmium and arsenic. 10 g of the ZLR was ground with a mortar and pestle, mixed with iron (III) sulphate in a crucible, covered and roasted in a muffle furnace. The roasted residue was subsequently leached with water at a controlled temperature. The mixture was filtered and the leachate was analysed with ICP. At room temperature, recoveries of 92.4%, 93.3%, 99.3%, 91.4% and 1.1% were obtained for Zn, Mn, Cu, Cd and Fe respectively. While the leaching process was carried out at different temperatures, room temperature (25 °C) was found to be the optimal temperature.

Mohan and Chander¹²⁷ investigated the recovery of iron, manganese, zinc and calcium from AMD using lignite, a low cost sorbent. The removal of Fe(II), Fe(III), Mn and Ca was studied in a batch mode at different pH levels. The pH was adjusted by the addition of H₂SO₄ and NaOH while constantly monitoring the pH with a pH meter. A stock solution with 100 ppm Fe(II) and Mn(II) and 60 ppm Fe(III), 25 mL of this solution was added to 0.15 g of lignite followed by its agitation for 48 hours. The organic sorbent matter was destroyed by ashing. The ash was digested with an acid and the filtrate was analysed using ICP-OES while the LECO CHN analyser was used for the quantification of carbon, nitrogen and sulphur. The analysis results revealed the presence of 32.1% SiO₂, 13.4% Al₂O₃, 1.30% TiO₂, 17.2% CaO, 1.81% MgO, 1.81% MnO, 18.8% Fe₂O₃, 0.28% Na₂O, 0.23% K₂O, 0.14% BaO, 0.26% SrO, 55.56% C, 4.83% H, 1.14% N, 0.84% S. The sorption of Fe(II), Mn(II) and Fe(III) on lignite increased with increasing pH.

¹²⁶ G. Jiang, B. Peng, Y. Liang, L. Chai, Q. Wang, Q. Li, M. Hu. (2017). "Recovery of valuable metals from zinc leaching residue by sulphate roasting and water leaching", *Transitions of nonferrous metals society of China*, 27(5), pp.1180-1187

¹²⁷ D. Mohan, S. Chander. (2006). "Removal and recovery of metal ions from acid mine drainage using lignite-alow cost sorbent", *Journal of hazardous materials*, 137(3), pp.1545-1553

Mohammadi *et al*¹²⁸ carried out the extraction of rubidium from waste samples obtained from a gold processing plant in Iran. This was achieved through a three-step process of acid washing, salt roasting and subsequent water leaching. Six samples of tailings were collected from a tailings dam at the depth of about 2 m, dry-sieved and quantified by ICP-OES and ICP -MS. The samples were roasted in a muffle furnace at elevated temperatures ranging between 500 and 950 °C. At ambient temperature, water leaching was carried out at the liquid-to-solid ratio of 1:1 for 30 minutes, followed by filtration. For the roasting part of the study, Na₂SO₄, NaCl and CaCO₃ were used as sulphation, chlorination and carbonation agents respectively, while CaCl₂•2H₂O was used as a sintering agent at different mass ratios. The results are reported in **Table 3.16**. The efficiency of Rb recovery was observed to be the largest with the: tailings/Na₂SO₄/CaCl₂•2H₂O ratio of 1: 0.1: 0.5. The same ratio worked best for the other reagents (NaCl and CaCO₃)

Table 3.16: Rb extraction efficiency at different ratios and reagents

| Mixture | Mass ratio | Rb extraction (%) |
|--|------------|-------------------|
| Tailings/Na ₂ SO ₄ /CaCl ₂ •2H ₂ O | 1:0.1:0.5 | 85.11 |
| | 1:0.25:0.5 | 68.21 |
| | 1:0.5:0.5 | 44.14 |
| | 1:0.5:0.25 | 36.76 |
| Tailings/NaCl/CaCl ₂ •2H ₂ O | 1:0.1:0.5 | 82.08 |
| | 1:0.25:0.5 | 61.98 |
| | 1:0.5:0.5 | 38.77 |
| | 1:0.5:0.25 | 29.13 |
| Tailings/CaCO ₃ /CaCl ₂ •2H ₂ O | 1:0.1:0.5 | 44.78 |
| | 1:0.25:0.5 | 38.54 |
| | 1:0.5:0.5 | 30.04 |
| | 1:0.5:0.25 | 23.26 |

¹²⁸ M. R. T. Mohammadi, S. M. J. Koleini, S. Javanshir, H. Abolghasemi, M. Abdollahy. (2015). "Extraction of rubidium from gold waste: process optimization", *Hydrometallurgy*, 151, pp.25-32

Santos and Ladeira¹²⁹ investigated the recovery of uranium from mine waste by leaching the samples with carbonate-based reagents, which included sodium carbonate (Na_2CO_3) and sodium bicarbonate (NaHCO_3). Sludge samples collected from a closed mine in Brazil were oven-dried at 50 °C for 24 hours, milled and sieved. Concentrations of Na_2CO_3 solutions ranged from 0.25 to 1.00 M while those of NaHCO_3 varied between 0.25 and 1.25 M. Solutions containing both the reagents were also used, in which the Na_2CO_3 concentration was in the range 0.25 to 2.50 M while the concentration of NaHCO_3 was kept constant at 0.25 M to determine the effect of Na_2CO_3 . Likewise, the effect of NaHCO_3 was investigated by varying its concentration from 0.55 to 1.15 M while that of Na_2CO_3 was set at 0.5 M. The sludge was found to contain 0.25% U_3O_8 , which is in the content in vein ores. The sludge can be used as a potential source of uranium. A 100% U recovery was achieved independent of the NaHCO_3 concentration by leaching for 48 hours.

3.7 ION EXCHANGE CHROMATOGRAPHY

Nascimento *et al*¹³⁰ carried out the recovery of uranium from acid mine drainage from the Caldas uranium mining and extraction plant in Brazil, using ion exchange chromatography. Amberlite Ira, a commercial strong base macro-porous resin, was used in this study. For the sorption tests, about 40 mL of the resin was packed in glass columns with a length of 50 cm and a 3 cm diameter. The feeding samples were stored in an 800 L capacity tank and the eluent was introduced into the columns in an up-flow manner while keeping the flow between the tank and columns constant, using a metering pump. Elution studies were carried out, using glass columns of length 40 cm and diameter 2 cm and the columns were packed to 20 mL heights with the resin. **Figure 3.3** illustrates the assembly of the system. Elution was carried out using 1.5 M NaCl at a 14 minute retention time. Approximately 98% of the

¹²⁹ E. A. Santos, A. C. Q. Ladeira. (2011). "Recovery of uranium from mine waste by leaching with carbonate-based reagents", *Environmental science and technology*, 45, pp.3591-3597

¹³⁰ M. R. L. Nascimento, O. Fatibello-Filho, L. A. Teuxeira. (2010). "Recovery of uranium from acid mine drainage waters by ion exchange", *Mineral processing and extractive metallurgy review*, 25(4), pp.129-142

uranium was successfully removed from the resin bed, with a 94% uranium removal from the AMD.

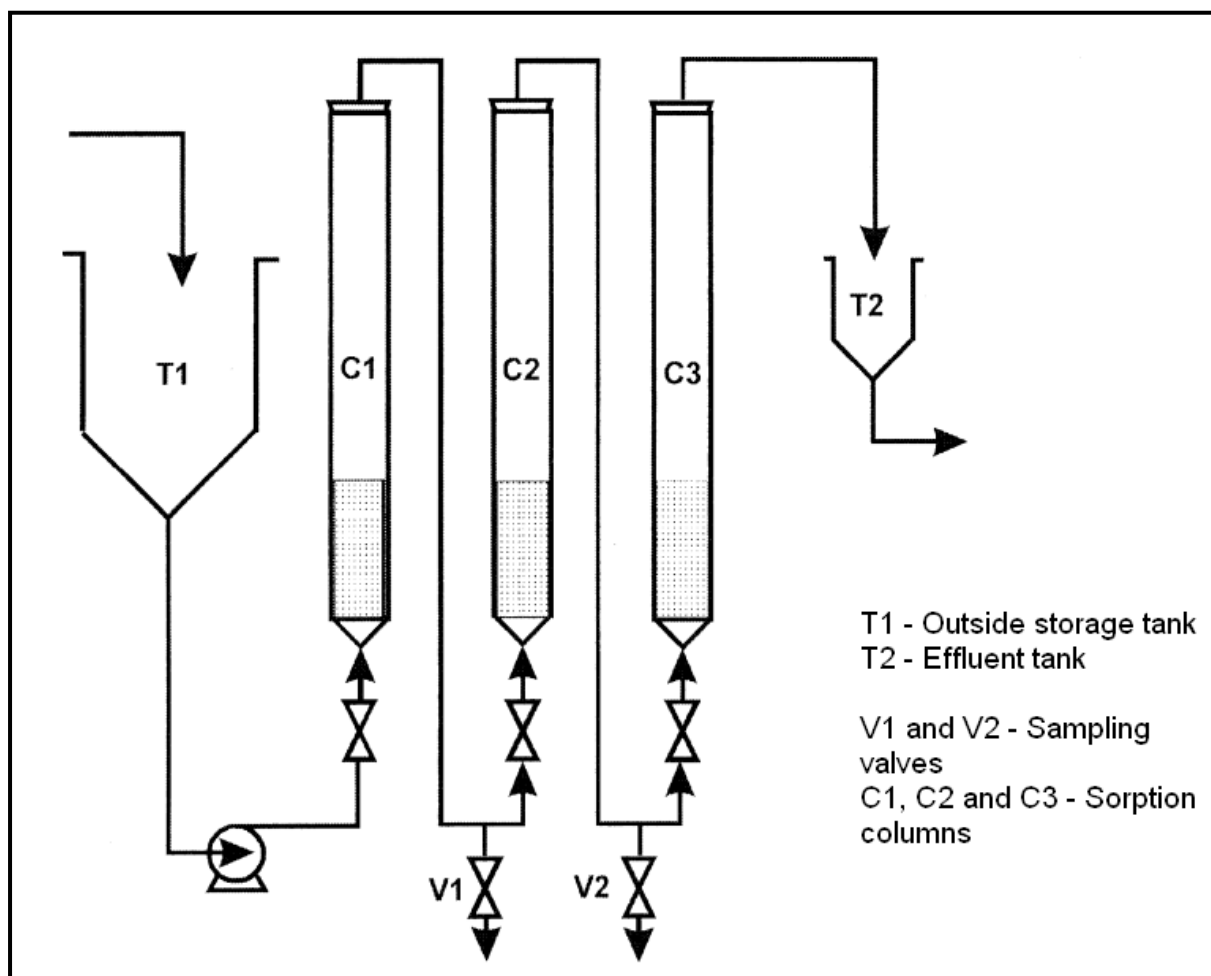


Figure 3.3: The laboratory assembly for continuous ion exchange sorption tests¹³⁰

Ladeira and Sicupira¹³¹ devised a simpler and more efficient ion exchange method for the recovery of uranium from AMD in Brazil. Two samples, A and B, were collected from two different dams at an abandoned mine (for longer than 20 years). The U concentrations were initially determined, by X-ray fluorescence and inductively coupled plasma mass spectrometry (ICP-MS), while the iron and sulphate concentrations were determined by AAS and EDS respectively. Glass columns were loaded with 15 mL of three different strong base resins, namely Amberlite IRA910U,

¹³¹ A. C. Q. Ladeira, L. C. Sicupira. (2013). "Application of ion exchange resins to recover uranium from mine drainage", *Proceedings of the 13th international conference of environmental science and technology*, Athens, Greece

Dowex MSA-2 and Dowex RPU. A downstream operation was performed, using a peristaltic pump at a flow rate of 2.5 mL/min at 25 °C. The initial concentrations of U in the two effluents were 8 and 11 mg/L respectively. Elution of the first sample was carried out by use of 0.1 M H₂SO₄ to elute iron as the first species, followed by a solution of 1.5 M NaCl and 0.05 M H₂SO₄. For the second sample, only 1.5 M NaCl was used as eluent. Amberlite IRA 910 U, Dowex MSA and Dowex RPU resulted in U recoveries of 89.7%, 70.15% and 99.7% respectively from the first sample and 86.6%, 94.1% and 92.7% from the second sample.

Monteagudo and Ortiz¹³² used ion-exchange to remove inorganic mercury from mine waste water streams. Several commercial resins were evaluated as possible ion exchangers and included Dowex XVS/M, Amberlite 252/M and Dowex XZS. The waste water sample was supplied by the Almadény and Arrayanes SA mines in Spain. The mercury concentration initially amounted to about 80 ppm while the waste samples also contained 522 ppm aluminium, 2 ppm arsenic, 42 ppm chromium, 843 ppm iron, 16 ppm manganese, 37 ppm nickel and 13 ppm zinc. The waste water in a storage tank was acidified prior to the Hg²⁺ ion removal. The solution was filtered using a 0.2 µm cartridge filter in order to remove any floating insoluble matter. The filtered water was subsequently treated with the ion exchange resins, reducing the mercury content of the waste water to about 34 ppb and the study proved that the Dowex XZS-1 had the highest selectivity for the mercury in these samples.

3.8 SOLVENT EXTRACTION

Although literature shows almost no proof of the use of solvent extraction in recovery of metals from mine waste, it has been successfully used in extraction of elements from other forms of industrial waste. It is therefore also considered as a possible method of treating mine waste samples.

¹³² J. M. Monteagudo, M. J. Ortiz. (2000). "Removal of inorganic mercury from mine waste water by ion exchange", *Journal of Chemical technology and biotechnology*, 75(9), pp.767–772

Li *et al*¹³³ succeeded in the selective recovery of heavy metals from waste water using synergistic solvent extraction. A synthetic aqueous solution was prepared by dissolving metal sulphate salts of analytical grade in deionised water. The synergistic organic system comprised 0.5 M Versatic 10 (2-methyl-2-ethylheptanoic acid) and 0.5 M Mextral 984H (a mixture of 2-hydroxy-5-nonyl-acetophenone oxime and 5-nonyl-salicylaldoxime) in Mextral DT100. The chemical composition of the synthetic solution is outlined in **Table 3.17**.

Table 3.17: The composition of the feed synthetic solution

| Concentration (mg/L) | | | | | | pH |
|----------------------|-------|---------|-------|-------|----------|-----|
| Cu | Ni | Zn | Cd | Ca | Mg | |
| 1 803.6 | 507.5 | 5 288.5 | 736.7 | 481.4 | 11 084.6 | 3.3 |

In glass bottles, NaOH solution was added in a drop-wise manner to adjust pH, and the two phases were mixed to reach an equilibrium point. The phases were then separated, and the raffinate was analysed by ICP-OES. After adjusting pH to 2.0 at a temperature of 40 °C, the copper was extracted preferentially with a recovery of more than 99%. When the pH was adjusted to 4.2 at 40 °C, the nickel was extracted next with a >98% recovery while the zinc and cadmium in the raffinate were extracted at the pH of about 6.5.

Tran *et al*¹³⁴ extracted thorium selectively from an acidic aqueous solution of a pH range of 4 - 6 using ortho ester tetraazophenylcalix[4]arene (TEAC) and chloroform was used as the organic solvent. In the study, 5 mL of an acetate buffer solution was added to 2 mL of Th(IV) 10^{-4} M in an aqueous solution. 5 mL TEAC dissolved in methanol with a concentration of 5×10^{-4} M was added to the Th solution and the pH of the mixture was adjusted to between 4 and 5 with HNO₃ and NaOH. The complex solution was further diluted by the addition of methanol: water mixture (ratio 7:3) to yield a final volume of 25 mL. A 5 mL aliquot of chloroform was added to the Th-

¹³³ Y. Li, L. Yang, Z. Xu, Q. Sun. (2017). "Separation and recovery of heavy metals from waste water using synergistic solvent extraction", *Material Sciences and engineering*, 167

¹³⁴ Q. H. Tran, V. T. Le, V. C. Nguyen. (2016). "Solvent extraction of thorium using 5,11,17,23-tetra[(2-ethylacetoethoxyphenyl)(azo)phenyl]calyx[4]arene", *Journal of chemistry*,

containing mixture which was shaken for 5 minutes at room temperature. After separation of phases, 1 g anhydrous Na_2SO_4 was added. Standards were prepared and the Th(IV) content was determined, using a UV-Vis spectrophotometer at 525 nm. Results indicated that a 98% extraction was achieved with the chloroform.

3.9 ELECTROWINNING

This is one of the most widely used techniques in modern metal recovery, mining, refining and waste water treatment. It was first introduced in 1807, although it was not commercially adopted until 1873,¹³⁵ and was mainly used in the recovery of gold and copper, amongst other metals. Since then, significant improvements and changes have been made to the original method.

Gorgievski *et al*¹³⁶ studied the recovery of copper from AMD produced at a closed mine, Cerovo, in Serbia by electrowinning. Samples of AMD were collected from two nearby springs and mixed to determine average metal concentrations in the water samples. The AMD had an initial copper concentration of 1.3 g/L and a pH of 3.52. A hydrodynamic circuit was built, using a reservoir, centrifugal pump, valves, a flow-meter and a cell. These were connected with plastic hose-pipes. The electrical components of the circuit comprised a power supply unit and a voltmeter, connecting wires and electrodes. A stainless steel grid was used as the anode, while three different cathodes were used, namely a flat copper plate, a porous copper sheet and a carbon felt. It was found that the use of the carbon felt and copper plate resulted in similar rates of Cu deposition, although the deposition on the copper plate was in the form of powder, and this led to termination. On the other hand, a good, dense Cu

¹³⁵ Electrowinning 101: What is electrowinning?. [Accessed 27-07-2018]. Available at: <https://blog.emew.com/electrowinning-101-what-is-electrowinning>

¹³⁵ M. Gorgievski, D. Bozic, V. Stankovic, G. Bogdanovic. (2009). "Copper electrowinning from acid mine drainage: a case study from the closed mine "Cerovo", *Journal of hazardous materials*, 170(2-3), pp.716-721

¹³⁶ M. Gorgievski, D. Bozic, V. Stankovic, G. Bogdanovic. (2009). "Copper electrowinning from acid mine drainage: a case study from the closed mine "Cerovo", *Journal of hazardous materials*, 170(2-3), pp.716-721

deposit was obtained which attached firmly to the carbon fibres. The use of a porous copper sheet resulted in the highest rate of Cu deposition at the lowest current, thus proving to be the best cathode amongst the three cathode types investigated. The concentration of copper in the resultant solution was found to be 0.1 g/L, thus giving a Cu recovery of over 92%.

Macingova *et al*¹³⁷ recovered manganese from AMD by electro-winning. The mine water samples were collected from a mine shaft, Pech in Slovakia, into which water draining from Smolnik deposits flows. The pH and Mn concentrations were found to be in the ranges 3.5 - 3.9 and 18 - 35 mg/L respectively. A synthetic solution with a pH 3.8 and Mn concentration 21.33 mg/L, (resembling the AMD in composition) was also prepared with the relevant metals' salts and used in the electro-winning process investigation. Nitric acid was added to oxidise iron (II) to iron (III), followed by the addition of sodium hydroxide to increase the pH to 4.0 in order to precipitate aluminium and iron by 94% and 99% respectively to avoid possible interferences. After filtration, electrolysis was carried out under conditions summarised in **Table 3.18**. Manganese was deposited to the anode as MnO₂ while a small fraction was deposited to the cathode as Mn. A Mn recovery of over 95% with a purity of 99% resulted, as determined by ICP-MS and XRF respectively.

Table 3.18: The experimental conditions of anodic electrodeposition¹³⁷

| Parameter | Value |
|------------------------|---------------|
| Anode vs SCE (V) | 1.3 - 1.9 |
| Cell voltage (V) | 2.3 - 2.9 |
| Current intensity (A) | 1 000 - 1 600 |
| Bath temperature (° C) | 90 |
| Electrolysis time (h) | 3 |

¹³⁷ E. Macingova, S. Ubaldini, A. Liptakova. (2016). "Study of manganese removal in the process of mine water remediation", *Journal of the Polish mineral engineering society*, pp.121-127

3.10 CONCLUSION

The largest mineral resources and mine waste dump sites, in the world by value are found in South Africa, and this qualifies the country as a producer of significant amounts of different commodities.¹³⁸ The exploration of waste beneficiation can add to the production at large with a potential economic boost for the country. It can also deal with some constraints which include the labour-intensive and expensive excavation costs. The literature survey has revealed that very little research has been done on mine waste beneficiation in the world. The research and investment, other than in gold recovery, in South Africa are even less and this leaves room for extensive research on the topic. The recycling of valuable elements present in the waste should be encouraged, as some successful research has already indicated the potential of the recovery of these metals from these neglected sources. Mine waste may contain elements that could be very useful for the industry and in everyday applications. The recovery of some elements from these sources has been successful in other parts of the world at high percent recoveries and should also be conducted in South Africa.

¹³⁸ M. Dworzanowski. (2013). "The role of metallurgy in enhancing beneficiation in the South African mining industry", *The journal of the Southern African institute of mining and metallurgy*, 113, pp.677-683

4 SELECTION OF ANALYTICAL AND SEPARATION TECHNIQUES

4.1 INTRODUCTION

The possible beneficiation of valuable elements from mineral ores and waste requires the use of different quantification and separation techniques. The categories of techniques which can be applied to achieve hydrometallurgical beneficiation include solid sample digestion, separation methods such as ion exchange chromatography and solvent extraction, while the success of each step in the process can be followed by different quantification techniques which may include AAS and ICP-OES/MS among others. It is important to ensure that the choice of method used for the preparation of samples is fully compatible with the method which will be used for qualitative and quantitative analyses. For example, ICP-OES analysis normally requires a sample in a liquid phase, and this in turn requires the complete dissolution of a solid sample.

The determination of the composition of a sample or chemical characterisation is a pre-requisite for the beneficiation of the samples. This step gives vital information on the type and quantity of the different elements in the sample. Numerous techniques such as XRF, SEM-EDS and XRD (powder diffraction) which do not require the dissolution of the sample, may be used to obtain valuable information in the elemental matrix of a sample, prior to its complete dissolution and subsequent beneficiation. There is also a range of methods which may be used for the separation and isolation of the different elements, but the selectivity, and hence the success of the separation and isolation steps, is dependent on the similarities and differences of the chemistry of the different elements present in the sample. In samples such as mine waste samples, selectivity is of paramount importance, particularly due to the large number of valuable elements present in these samples. This chapter covers the

methods that have been employed in the study for the sample digestion, characterisation, separation and isolation as well as elemental quantification.

4.2 SAMPLE DISSOLUTION

In order to characterise the sample completely for its chemical composition, the sample must be converted into a compatible form to allow the analysis. Most instruments which are used in the accurate chemical analysis require the conversion of solid samples into solutions. This is a very important step and must be carried out with great care as the sample preparation procedure influences the accuracy of the results more than the applied analytical technique. It is even more important to ensure that the sample which is to be analysed represents the collective sample and that care is taken to minimise/prevent any loss of matter while preparing/dissolving the sample.¹³⁹

Digestion is normally carried out using a technique that is either selective towards the elements of interest or dissolves the sample completely. Samples are usually ground into fine particles to increase the surface area and thus increase the rate of the dissolution reaction by exposing it to the reagents used. This also makes it easier to homogenise.

The digestion of solid samples such as mineral ores and solid mine waste can be a very daunting task due to the uncertainty of the chemical composition of these samples. For example, a mineral ore sample is usually a combination of different minerals which complicates the dissolution process. The dissolution of mine waste rock and tailings resembles that of the mineral ores since these products were initially also rock or solid natural material excavated from the earth.

¹³⁹ United States environmental protection agency. (2004). Laboratory sample preparation, Marlap manual, 2(12), p.1

However, the actual dissolution efficiency depends mainly on the chemical composition of a material. Elements normally occur in nature as oxides, phosphates, carbonates, sulphides or as combinations due to the presence of different elements in these samples. The elements themselves may also have different oxidation states in the solid samples which may require different dissolution techniques. The most popular or effective solid sample dissolution techniques are wet ashing (mineral acids) or flux fusion (alkali salts).

4.2.1 WET ASHING OR ACID DIGESTION

Simpler solid samples can effectively be digested using mineral acids. In this dissolution technique, it is important to ensure that the acid of choice must not only be compatible with the method of analysis but also that it should not dissolve the materials with which it comes into contact, such as the crucible or other type of container used in the dissolution step.¹⁴⁰ In an ideal situation, the acid of choice must dissolve the sample completely. Non-oxidising acids include dilute hydrofluoric, hydrochloric and sulphuric acids which dissolve the elements which are normally present as metal oxides or carbonates in a simple acid-base reaction to generate hydrated metal ions in solution. On the other hand, oxidising acids include hot concentrated perchloric and nitric acids.¹⁴¹ In these types of dissolution reactions, the elements within the solid samples are converted to water-soluble oxidation states. Although most of the acid reactions are exothermic, application of heat is usually encouraged or employed, which produces additional convection currents in the solution and it also increases the rate of dissolution reactions (kinetic considerations). The loss of reactive species may be prevented by use of a reflux arrangement, so that constant azeotropes are continuously returned to the reaction vessel.¹⁴²

¹⁴⁰ E. Prichard, G. M. Mackay, J. Points. (1996). Trace analysis, a structured approach to obtaining reliable results, *Royal society of chemistry*, p.65

¹⁴¹ R. M. Twyman. (2005). "Sample dissolution for elemental analysis: wet digestion". Encyclopedia of analytical science, 2nd ed., (8), London, *Elsevier science*, pp.146-153

¹⁴² T. R. Dulski. (1996). A manual for the chemical analysis of metals, MNL 25, Ann Arbor, *American society for testing and materials*, pp.70-96

Nitric acid is an oxidising acid which may be used for almost all matrix types, except in samples which contain large amounts of organic material which may easily be converted to explosive substances with the nitrification of reactive organic molecules. The power of nitric acid as a dissolution agent is in its ability to act as both an oxidising reagent and a strong acid which converts the elements in solid samples either by oxidation or by acid/base reactions into water-soluble salts, while it also decomposes organic compounds to form water and carbon dioxide as products.¹⁴³ Although it does not dissolve most oxides effectively, HNO_3 can dissolve the oxides of thorium and those of uranium and simultaneously oxidise U^{4+} to U^{6+} .¹⁴⁴ It may also be used in the presence of ozone to enhance the digestion. In its concentrated form, nitric acid can decompose carbonate and sulphide minerals. It is, therefore, used in rock analysis for the determination of sulphur and for extraction and determination of heavy metals which occur as the sulphides in a silicate matrix.¹⁴⁵ On the downside, it forms insoluble oxides of Nb, Ta, Sb, Ti, Sn, Al, and W.

Hydrochloric acid is mainly used on inorganic matrices. However, it often forms insoluble chlorides in the presence of Pb, Ag, Hg and Tl and forms volatile chlorides of Hg, Ge, As, Sb and Se. It works well on metal oxides and metals which are more easily oxidised compared to hydrogen. It also dissolves most phosphates, carbonates and sulphides except pyrite. On heating, the hydrogen chloride gas escapes and the HCl concentration decreases rapidly at temperatures exceeding its boiling point of about 110 °C.¹⁴⁶

Sulphuric acid is also used to dissolve many materials, especially when used at its boiling point (about 338 °C). This makes it an acid of choice to dissolve solid samples resistant to dissolution. Sulphuric acid is not very effective in dissolving rocks and

¹⁴³ M. A. Z. Arruda. (2007). Trends in sample preparation, UK ed., *Nova science publishers Inc.*, p.89

¹⁴⁴ E. Zimmer, E. Merz. (1984). "Dissolution of thorium-uranium mixed oxides in concentrated nitric acid", *Journal of nuclear materials*, 124, pp.64-67

¹⁴⁵ P. G. Jeffery, D. Hutchison. (1981). Chemical methods of rock analysis, 3rd ed., Oxford, *Pergamon press*, p.18

¹⁴⁶ D. A. Skoog, D. M. West, F. J. Holler, S. R. Crouch, (2014). Fundamentals of analytical chemistry, 9th ed., *Brooks/Cole, Cengage learning*, p.978

minerals containing elements which can form insoluble sulphates. It is, likewise, ineffective as oxidising agent. However, it is effective in the decomposition of phosphate, sulphide and fluoride minerals, especially monazite¹⁴⁷, which contains numerous REEs.

Phosphoric (orthophosphoric) acid may be used to decompose metal oxides as well as silicate minerals at an elevated temperature.¹⁴⁸ It may be used for the determination of free silica in the presence of silicates, based on the different solubility of free silica from that of silicates in hot H_3PO_4 , as a very easy method without the need for any special apparatus and techniques.¹⁴⁹ The heating of the orthophosphoric acid in the range of 220 °C to 250 °C converts it to pyrophosphoric acid, thus improving the dissolution ability.

Aqua-regia, a mixture of HCl and HNO_3 , usually three parts of the former and one part of the latter by volume, may also be used in the digestion.¹⁵⁰ A mixture of acids usually dissolves a larger number of elements from a rock sample compared to using individual acids. This acid mixture produces chlorine and nitrosyl chloride in-situ which accounts for its powerful dissolution properties, but must be used while still fresh, as the chlorine and nitrosyl chloride (gases) escape from the solution and thus reducing the dissolution ability of the acid. Aqua-regia has been used in the dissolution of noble metals including platinum and gold.^{151,152}

¹⁴⁷ R. D. Abreu, C. A. Morais. (2010). "Purification of rare earth elements from monazite sulphuric acid leach liquor and the production of high-purity ceric oxide", *Minerals engineering*, 23(6), pp.536-540

¹⁴⁸ N. A. Talvitie. (1951). "Determination of quartz in presence of silicates using phosphoric acid", *Analytical chemistry*, 23(4), pp.623-626

¹⁴⁹ A. Hamada. (1964). "Determination of free silica by phosphoric acid method", *Industrial health*, 2, pp.181-188

¹⁵⁰ B. D. Craig, D. B. Anderson. (1995). Handbook of corrosion data, 2nd ed., England, ASM international, p.166

¹⁵¹ A. L. Mular, D. N. Halbe, D. J. Barratt. (2002). Mineral processing plant design, practice and control: proceedings, 2, p.1767

¹⁵² M. Chen, L. Q. Ma. (2001). "Comparison of three aqua regia digestion methods for twenty Florida soils", *Soil science society of America journal*, 65, pp.491-499

Another important acid at the disposal of researchers for mineral dissolution is hydrofluoric acid (HF) and this may be used for the dissolution of metal silicates, aluminosilicates and oxides. The effectiveness of dissolution with HF increases with an increase in temperature.¹⁵³ An advantage of using HF is the formation of the volatile silicon tetrafluoride (SiF₄) which decreases the total dissolved solids and therefore influences the analysis positively. However, HF is a very dangerous acid to humans. It penetrates tissue, and reacts with blood calcium and can cause cardiac arrest. Other possible effects of exposure include rhinitis, bronchitis and bone damage. Care must be taken to avoid any contact with the skin and any inhalation.¹⁵⁴

4.2.2 FLUX FUSION

Flux fusion is the dissolution of a sample by using a molten inorganic salt, called a flux, at a relatively high temperature.¹⁵⁵ This technique is usually used for materials which do not dissolve completely in mineral acids. In this process, the molten flux acts as an ionic solvent while the sample remains in its solid state.¹⁵⁶ Advantages of using the molten salts as dissolution agents include the high reaction temperatures and very high reagent concentrations while the normal reactions (which include acid-base, red-ox and complex formation) take place in these ionic liquids. Successful fusion requires that the liquid mixture of the sample and the flux forms a homogenous solid upon cooling. Flux fusion is ideal for rocks and minerals containing sulphides, silicates, phosphates, carbonates, sulphates, oxides and refractory minerals.¹⁵⁷ Of all the alkali metals present in many fluxes, the lithium salts are usually the best because their products are the most soluble in water while lithium has relatively few

¹⁵³ Z. B. Alfassi. (1998). Instrumental multi-element chemical analysis, Dordrecht, *Springer science + Business media*, p.2

¹⁵⁴ J. C. Bertolini. (1992). "Hydrofluoric acid: a review of toxicity", *The journal of emergency medicine*, 10(2), pp.163-168

¹⁵⁵ J. Kenkel. (2013). Analytical chemistry for technicians, 4th ed, CRC press, *Taylor & Francis Group*, p.30

¹⁵⁶ Inorganic sample preparation by fusion for XRF, AA and ICP analysis. [Accessed 09-02-2018]. Available at: <http://www.katanax.com/cgi/show.cgi?aboutfusion.l=en.html>

¹⁵⁷ B. K. Sharma. (2006). Analytical chemistry, 2nd ed., Meerut, Delhi, *Krishna Prakashan media(P) Ltd.*, p.40

spectral lines which decrease the probability of spectral interference during quantification using equipment such as ICP-OES.¹⁵⁸ However, it is important to note that the chemistry of lithium compounds is very different when compared to that of the other compounds of alkali metals. For example, Na_2CO_3 works well with a platinum crucible, whereas Li_2CO_3 attacks the crucible due to the metal's reactivity towards platinum. Some commonly used fluxes are presented in **Table 4.1** with the conditions of their application.

Table 4.1: Some common fluxes and their application^{157,159}

| Non-oxidising fluxes | | |
|--|---------------|---|
| Flux | Crucible type | Applications |
| Na_2CO_3 | Pt | Silicates, phosphates, sulphates |
| NaOH or KOH | Au, Ni, Ag | Silicates, silicon carbides |
| B_2O_3 | Pt | Silicates, oxides |
| $\text{Li}_2\text{B}_4\text{O}_7$ or LiBO_2 | Pt, graphite | Almost all materials except metals and sulphides. $\text{Li}_2\text{B}_4\text{O}_7$ works best on resistant silicates and basic oxides while LiBO_2 works better on acidic oxides. |
| CaCO_3 - NH_4Cl | Ni | Silicates, oxides |
| Oxidising fluxes | | |
| Na_2O_2 | Fe, Ni | Sulphides, acid-insoluble alloys, insoluble oxides, iron ore and Zr. |
| $\text{K}_2\text{S}_2\text{O}_7$ | Pt, Porcelain | Hf and Th phosphates |

Borate fusion is a popular technique which dissolves samples at 1050 °C or slightly higher.¹⁶⁰ This method may be applied to samples which are difficult to prepare as homogeneous products, such as glasses, ceramics, rocks (especially silicate rocks),

¹⁵⁸ P. Gaines. Sample preparation by fusion. [Accessed 22-02-2018]. Available at:

<https://www.inorganicventures.com/sample-preparation-fusion>

¹⁵⁹ Sample dissolution. [Accessed 14-01-2018]. Available at:

<https://www.epa.gov/sites/production/files/2015-05/documents/402-b-04-001b-13-final.pdf>

¹⁶⁰ G. P. Thomas. (2013). An introduction to borate fusion sample preparation. [Accessed 11-01-2018].

Available at: <https://www.azom.com/article.aspx?ArticleID=8770>,

sediments and ores. The products of borate fusion of these sample types are suitable to be separated and quantified with a wide range of analysis techniques.¹⁶¹ Moreover, the method gives rapid and complete decomposition of oxide minerals such as ilmenite, magnetite, rutile and perovskite. This method can also be used in combination with HF to recover REEs and thorium as insoluble fluorides.¹⁶² Lithium metaborate (LiBO_2) is one of the most common borate fluxes, followed by lithium tetraborate ($\text{Li}_2\text{B}_4\text{O}_7$), and these have replaced the previously widely used fluxes such as NaOH and Na_2CO_3 .¹⁶³

Sodium carbonate works well with almost every silicate sample. It is the most widely used flux for the decomposition of raw materials including silica and has found a major application in the fusion of silicate minerals. Although the melting point of this flux is 851 °C, the temperature of fusion is 852 °C because it begins to decompose by releasing CO_2 as product just below the melting point.¹⁴² Lithium carbonate is rarely used, although it is the best carbonate, with minimal spectral interference.

The advantages of fusion over other sample dissolution techniques include the absence of mineralogical, grain size and orientation effects, complete homogeneity of the melt and digestion of samples which are extremely difficult to dissolve.¹⁵⁶ Drawbacks associated with flux-fusion generally include fairly high quantity of the flux which is needed for sample dissolution and poses challenges in terms of the accurate quantification of the different elements due to possible spectral interference by the elements in the flux.¹⁶⁴ This also raises the amount of dissolved solids in the solution and increases the risk of salting out in the nebulisers of instruments such as

¹⁶¹ Borate fusion. [Accessed 01-03-2018]. Available at:

<https://www.spexsampleprep.com/techniques/borate-fusion>

¹⁶² P. G. Jeffery. (1957). "Decomposition of oxide minerals by fusion with borax", *Analyst*, 82(970), pp.66-67

¹⁶³ Z. Mester, R. E. Sturgeon. (2003). "Sample preparation for trace element analysis", *Comprehensive analytical chemistry*, 41, p. 751

¹⁶⁴ J. Kenkel. (1992). Analytical chemistry refresher manual, 1st ed., *CRC Press*, p.42

ICP-OES. Additionally, the flux might react with the crucible, thus creating contamination problems.¹⁶⁵

4.3 SPECTROSCOPIC TECHNIQUES

Spectroscopy is the study of the interaction of matter with electromagnetic radiation at any portion of the electromagnetic spectrum, a range of frequencies and wavelengths (**Figure 4.1**).¹⁶⁶ The interaction between the electromagnetic radiation and matter usually results in a spectrum which is then studied to deduce or obtain useful information about the matter. The spectra may be divided into two types, namely absorption and emission spectra, although a mathematical equation exists to convert the one to the other.¹⁶⁷ Electromagnetic radiation is a form of energy which has both wave- and particle-properties.

Spectroscopic techniques are very powerful in terms of quantifying all the different elements in a sample. The main advantage of these techniques is that they use the unique properties (fingerprinting) of each element to identify and quantify the elements. The advantages of these techniques over other classical techniques, such as titrimetry and gravimetry, include its ability to quantify an element irrespective of its chemical form in the sample, time efficiency, and minimal preparation of sample needed in some cases, high reproducibility and minimal human errors.¹⁶⁸ However, spectroscopic techniques used for solid sample analyses do not analyse properly if there is a significant variation in the chemical composition of the sample particles.

¹⁶⁵ J. Kenkel. (2010). Analytical chemistry for technicians, 3rd ed., *Lewis publishers*, p.28

¹⁶⁶ Spectroscopy definition and the difference from spectrometry. [Accessed 20-01-2018]. Available at: <https://www.thoughtco.com/definition-of-spectroscopy-605676>

¹⁶⁷ J. M. Hollas. (2002). Basic atomic and molecular spectroscopy, Cambridge, UK, *The royal society of chemistry*, p.1

¹⁶⁸ J. W. Robinson. (1996). Atomic spectroscopy, 2nd ed., New York, *Marcel Dekker inc.* pp.5-6

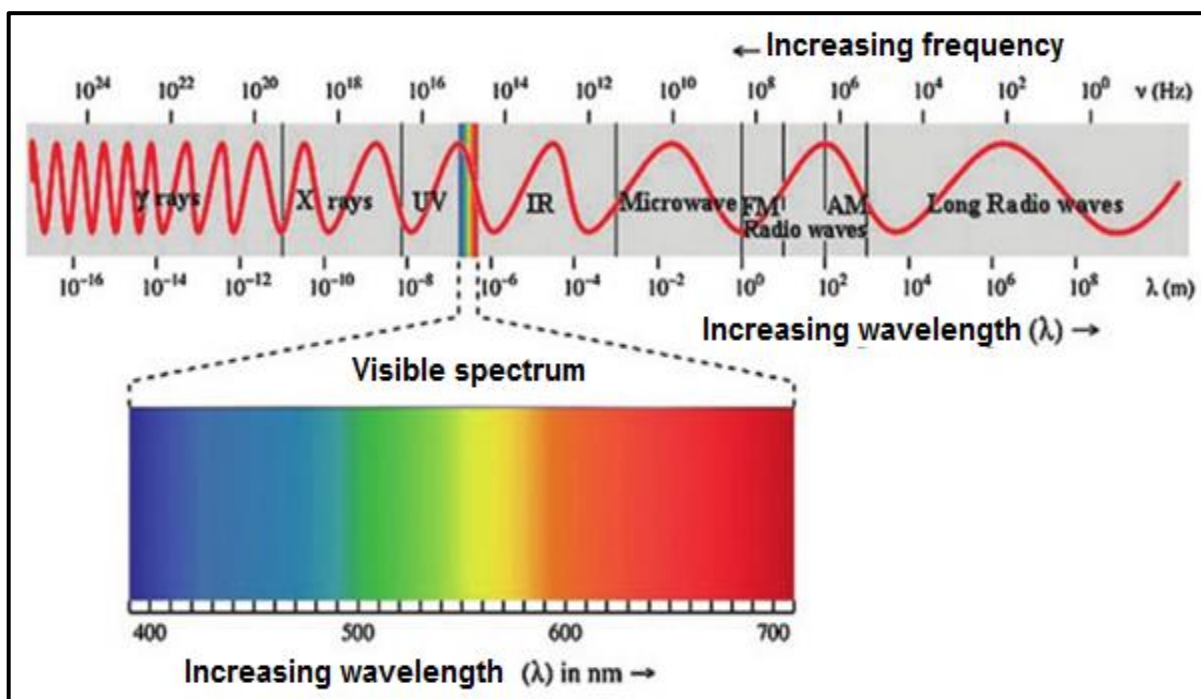


Figure 4.1: The electromagnetic spectrum¹⁶⁹

4.3.1 INDUCTIVELY COUPLED PLASMA OPTICAL EMISSION SPECTROSCOPY

The inductively coupled plasma optical emission spectroscopy (ICP-OES) is currently the most popular and most powerful method to identify and quantify elemental content. Its popularity stems from its ability to analyse almost all of the elements on the periodic table simultaneously, excellent detection limits and large dynamic linear range detection ability.

A graphic presentation of the functioning of an ICP-OES is depicted in **Figure 4.2**. A pumping system (peristaltic pump) introduces liquid samples, often as aqueous solutions, into the ICP. The sample solution is then converted into an aerosol by the nebuliser¹⁷⁰ and then re-directed into the channel of the plasma which operates at a temperature between 6 000 K and 10 000 K where the aerosol is vaporised. The

¹⁶⁹ A. Manickavasagan, H. Jayasuriya. (2014). Imaging with electromagnetic spectrum: applications in food and agriculture, *Springer-Verlag Berlin Heidelberg*, p.68

¹⁷⁰ J. Cazes. (2004). Analytical instrumentation handbook, 3rd ed., Florida, USA: *Taylor & Francis Group*, p.64

analyte in the solution is released as free atoms in the gaseous state.¹⁷¹ The atoms then gain further energy due to collision in the plasma and the valence electrons get excited in both atomic and ionic forms. The excited ions and atoms then emit light (photons) upon relaxation to their ground state, which is converted to an electrical signal by a photomultiplier in the spectrometer. The intensity of the electrical signal is compared to a previously measured intensity of a solution containing a known concentration of the analyte (standard solutions), and the concentration of the analyte in the sample is then calculated.¹⁷² The wavelengths of the photons which are emitted after the relaxation of electrons to the ground state is unique for every element on the periodic table, which allows for the identification of all the elements present in the specific sample. The number of photons emitted is directly proportional to the concentration of the element in consideration in the sample, which allows for the quantification of the elements.¹⁷³

¹⁷¹ X. Hou, B. T. Jones. (2000). Inductively coupled plasma /optical emission spectrometry, Encyclopedia of analytical chemistry, pp.9468-9485

¹⁷² M. Thompson, J. N. Walsh. (1989). Handbook of inductively coupled plasma spectrometry, 2nd ed., Blackie & Son Ltd

¹⁷³ R. Tantra. (2016). Nanomaterial characterization: an introduction, Hoboken, New Jersey, John Wiley & Sons, Inc., p.95

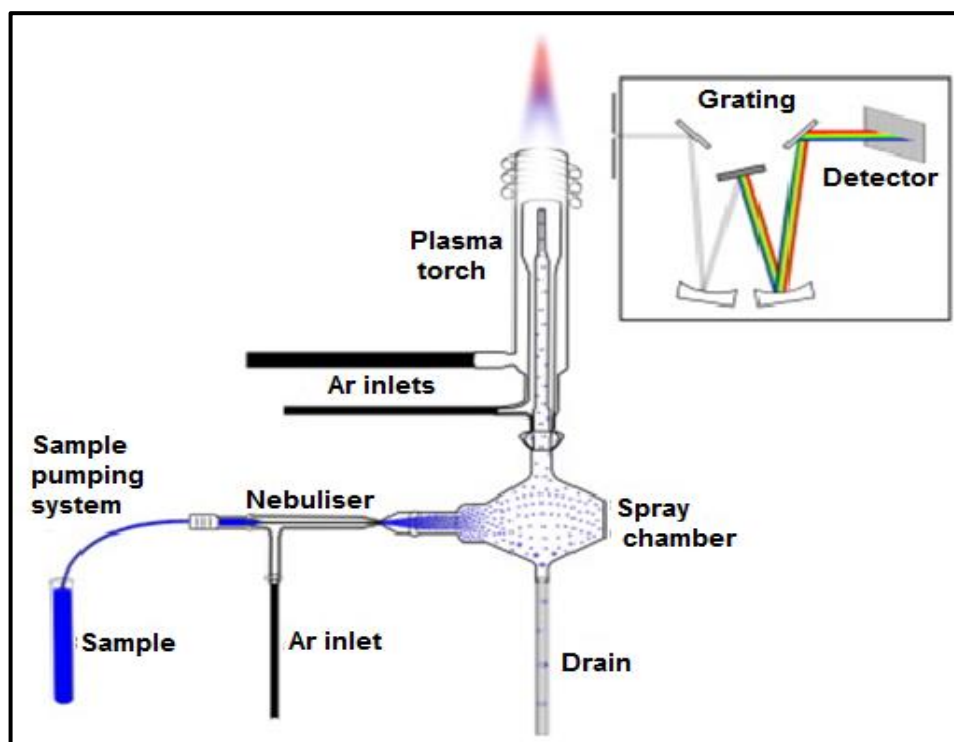


Figure 4.2: Operation of an ICP - OES instrument¹⁷⁴

As indicated previously, the advantages of ICP-OES include low detection limits which enable trace element analysis, simultaneous determination of different elements (over 70 elements), a wide dynamic linear range, good stability, high electron density and low chemical and matrix interference.¹⁷⁵ Additionally, the sensitivity is fairly good, the degree of ionisation is good for many elements and the data are handled easily.¹⁷¹ The shortcomings of this technique include spectral interferences from elements other than the analyte in the sample, the introduction of the sample in liquid state only, and a relatively high cost of the equipment. Furthermore, the sample introduction through pneumatic nebuliser has a low efficiency while the argon plasma has a low tolerance for organic solvents and high salt contents.¹⁷⁶

¹⁷⁴ F. Caruso, S. Mantellato, M. Palacios, R. J. Flatt. (2017). "ICP-OES method for the characterization of cement pore solutions and their modification by polycarboxylate-based superplasticizers", *Cement and concrete research*, 91, pp.52-60

¹⁷⁵ S. S. Nielsen. (2017). Food analysis, 5th ed., Switzerland, *Springer international publishing*, p.146

¹⁷⁶ R. A. Scott, C. M. Lukehart. (2007). Applications of physical methods to inorganic and bioinorganic chemistry, *John Wiley & Sons*, p.206

4.3.2 SCANNING ELECTRON MICROSCOPY ENERGY DISPERSIVE X-RAY SPECTROSCOPY (SEM-EDS)

Scanning electron microscopy energy dispersive X-ray spectroscopy (SEM-EDS) is a widely used technique in solid state elemental microanalysis for qualitative and quantitative analyses of all elements of the periodic table with the exception of H, He and Li.¹⁷⁷ This combination of instruments comprises an electron microscope as well as an energy dispersive X-ray spectrometer. The scanning electron microscope comprises an electron source, electron lenses, sample stage, solid-state detector, semiconductor and display monitor.¹⁷⁸ The instrument has very high magnification capabilities (up to 200 000 times) and produces images of the sample by the use of a focussed scanned electron beam. It is capable of generating images, not only of the sample's surface, but also those of its cross-sections.¹⁷⁹

Energy dispersive X-ray spectroscopy (EDS) is a micro-analytical technique that determines the qualitative and quantitative elemental composition of solid samples using electrons.¹⁸⁰ Bombardment of the sample by the electron beam in the SEM results in a release of electrons from the inner, or core orbitals of the atoms situated on the surface of the sample. The voids left by these electrons are filled up by higher energy electrons which cascade to the lower orbitals and emit X-rays equivalent to the difference between the two energy states. This energy, which is recorded by the EDS detector, is unique for each element. The detector converts this energy into the type and amount of elements present on the surface.¹⁸¹ The process is illustrated in **Figure 4.3**.

¹⁷⁷ D. E. Newbury, N. W. Ritchie. (2013). "Is scanning electron microscopy/energy dispersive x-ray spectrometry (SEM/EDS) quantitative?", *Scanning*, 35(3), pp.141-168

¹⁷⁸ Scanning electron microscopy (SEM) energy dispersive spectroscopy (EDS). [Accessed 11-05-2018]. Available at: <https://www.avomeen.com/news/articles/knowledge-center-white-papers/sem/eds/>

¹⁷⁹ SEM principle and instruments. [Accessed 09-05-2018]. Available at: https://www.lpdlabsservices.co.uk/analytical_techniques/sem/sem_instrument.php

¹⁸⁰ C. A. Andrei. (2017). Towards efficient photovoltaic devices: key facts and experiments on dye sensitised solar cells, 1st ed., *Cambridge scholars publishing*, p.47

¹⁸¹ J. C. Russ. (1984). Fundamentals of energy dispersive X-ray analysis, *Butterworths & Co(Publishers) Ltd.*, pp.18-19

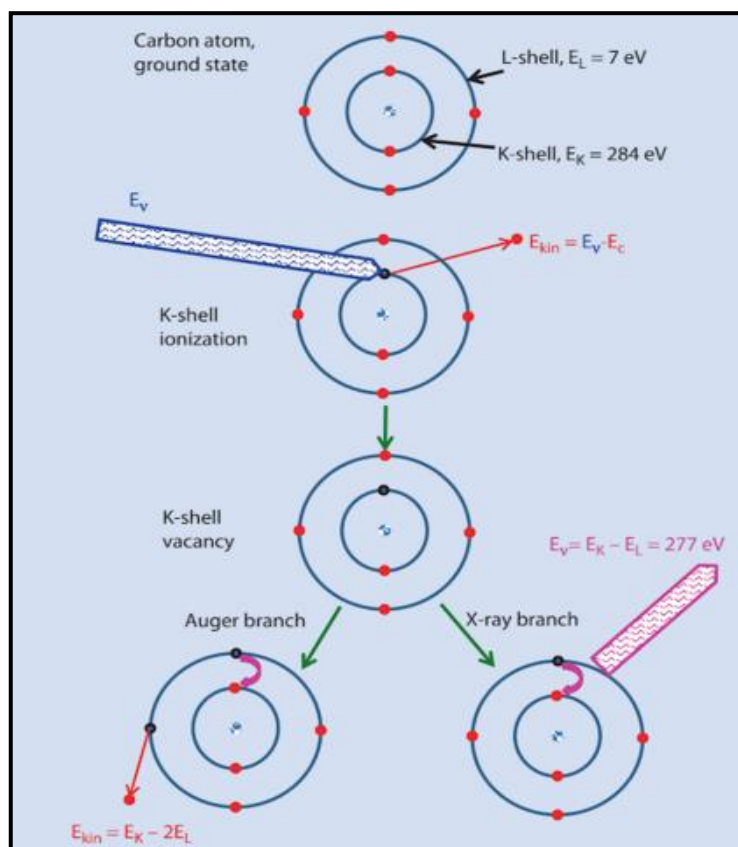


Figure 4.3: A schematic presentation of the generation of X-rays. The K-shell is the inner shell while the L-shell is the outer electron shell¹⁸²

The EDS detector (**Figure 4.4**) is usually based on a semiconductor device such as a silicon crystal. The collimator ensures collection of only the X-rays produced by the interaction of the incident electron beam with the sample. The electron trap attracts different types of scattered electrons, thus preventing them from entering further into the detector. A window isolates the detector crystal and keeps it under high vacuum. The charge recorded by the detector is converted into a voltage pulse by the electronic components which pass it to the pulse processor.¹⁸³

¹⁸² J. I. Goldstein, D. E. Newbury, J. R. Michael, N. W. M. Ritchie, J. H. J. Scott, D. C. Joy. (2018). Scanning electron microscopy and x-ray microanalysis, 4th ed., *Springer science+business media LLC*, p.54

¹⁸³ EDS principle. [Accessed 09-05-2018]. Available at: <https://ywcmatsci.yale.edu/edx-principle>

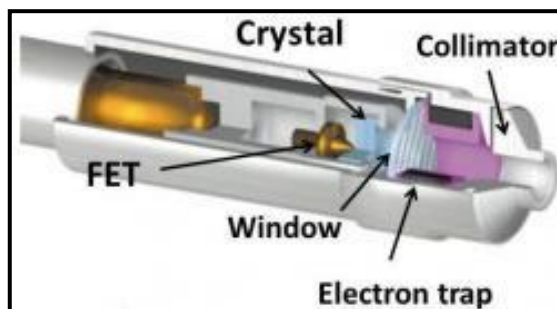


Figure 4.4: The EDS detector¹⁸³

In spot mode, a full elemental spectrum can be obtained in a few seconds by the aid of supporting software which facilitates the identification of peaks. Additionally, the chemical composition of samples can be determined, in semi-quantitative mode, by comparison of the peak-height of an element in the sample relative to a standard.¹⁸⁴ Furthermore, the equipment is quite easy to operate. The disadvantages include the high cost of the equipment, its bulky size and the need for housing of equipment away from any electric, magnetic or vibrational interference. Additionally, a high level of expertise is required for operation and sample preparation.¹⁸⁵ The technique involves destructive analysis in most cases and the signal-to-noise ratio is low.¹⁸⁶

4.4 HYDROMETALLURGICAL TECHNIQUES FOR RECOVERY OF VALUABLE ELEMENTS FROM WASTE

The recovery of elements from a matrix requires the use of methods that are capable of isolating the element of interest from the matrix. While some methods isolate by dissolving only the elements of interest from the solid sample, such as leaching, other

¹⁸⁴ D. Haberlah, M. Owen, P. W. S. K. Botha, P. Gottlieb. (2011). "SEM-EDS-based protocol for subsurface drilling mineral identification and petrological classification", *10th international congress for applied mineralogy*, Australia

¹⁸⁵ O. P. Choudhary, Priyanka. (2017). "Scanning electron microscope: advantages and disadvantages in imaging components", *International journal of current microbiology and applied sciences*, 6(5), pp.1877-1882

¹⁸⁶ Advantage and disadvantage of EDS technique. [Accessed 13-06-2018]. Available at: <http://www.globalsino.com/EM/page4661.html>

methods require prior complete dissolution of solid samples. Water samples are therefore easier to work with compared to solid samples as they need no dissolution step. Solid samples are easy to work on through leaching if the lixiviant is selective to the element of interest. The methods that were successfully applied to mine waste are covered in this section.

4.4.1 ADSORPTION

Adsorption is the adhesion of gas, liquid or dissolved solid particles (atoms, molecules or ions) onto other solid surfaces such as activated carbon, silica and graphene.¹⁸⁷ The substance that accumulates on the surface is the adsorbate while that which provides the surface is termed the adsorbent.¹⁸⁸ For a successful adsorption, the adsorbent must have a large surface area to accommodate the maximum amount of the particles of the adsorbate. A porous material works well as an adsorbent to attract organic and inorganic substances. This technique may be used to recover metals from aqueous solutions such as mine waste water, and can thus be used as a separation technique. A number of natural adsorbents such as fruit peels¹⁸⁹ are available and as an advantage, they are inexpensive. One of these is activated carbon, which can be used to adsorb organic molecules and non-polar adsorbates; it is also used to remove gold from aqueous solutions.¹⁹⁰

¹⁸⁷ M. Karnib, A. Kabbani, H. Holail, Z. Olama. (2014). "Heavy metals removal using activated carbon, silica and silica activated carbon composite", *Energy procedia*, 50, pp.113-120

¹⁸⁸ E. Furuya, K. E. Noll, J. Sohn, S. Lee, S. Yamashita, Y. Takeuchi. (1993). "Effect of functional groups on adsorption of organics dissolved in water onto macroreticular resin particles", *Proceedings of the fourth international conference on fundamentals of adsorption*, Kyoto May 1992, p.185

¹⁸⁹ R. Mallampati, L. Xuanjun, A. Adin, S. Valiyaveetil. (2015). "Fruit peels as efficient renewable adsorbents for removal of dissolved heavy metals and dyes from water", *American chemical society*, 3(6), pp.1117-1124

¹⁹⁰ W. Bunmahotama, W. Hung, T. Lin. (2018). "Simulation of the adsorption capacity of polar organic compounds and dyes from water onto activated carbons: model development and validation", *Sustainable environment research*, 28(2), pp.57-64

4.4.2 PRECIPITATION

Precipitation is also a very useful method in the separation of chemical compounds. Precipitation involves the selective formation of a solid from a solution. It is carried out by addition of a reagent which contains ions that form a sparingly soluble or insoluble salt with a target metal ion in the solution. The reagent which is added into the solution is termed the precipitant while the formed solid is called the precipitate.¹⁹¹ The precipitate may be crystalline and may be suspended in the liquid or may sink to the bottom. The liquid is called the supernatant liquid or supernate and it may be separated by filtration or decantation.¹⁹² If the precipitate is suspended throughout the liquid, centrifugation may be employed to make it possible to decant. **Figure 4.5** depicts the formation of a precipitate from a solution in which a precipitant is added.

¹⁹¹ Precipitation (chemistry). [Accessed 24-06-2018]. Available at:
[https://en.wikipedia.org/wiki/Precipitation_\(chemistry\)](https://en.wikipedia.org/wiki/Precipitation_(chemistry))

¹⁹² Precipitation reactions. [Accessed 25-06-2018]. Available at:
https://chem.libretexts.org/Core/Inorganic_Chemistry/Descriptive_Chemistry/Main_Group_Reactions/Reactions_in_Aqueous_Solutions/Precipitation_Reactions

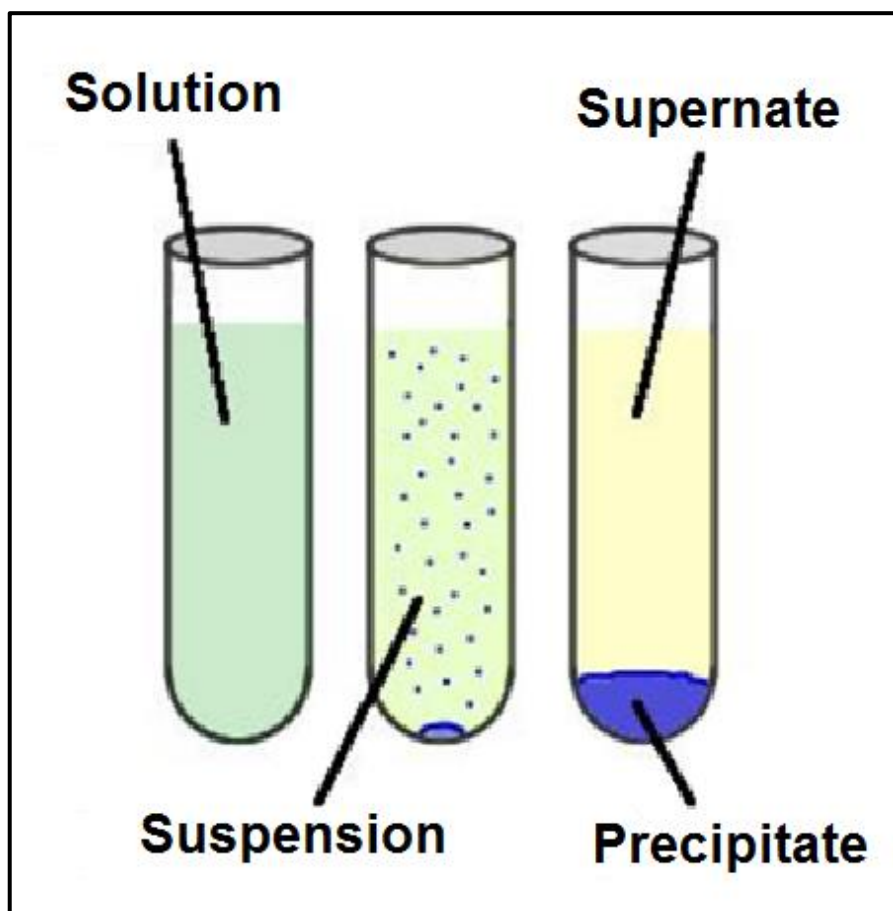


Figure 4.5: The formation of a precipitate from a solution¹⁹³

This is one of the major methods of separating an analyte (or metal of interest) from a solution. The metal ion can react with an anion to convert it into a sparingly soluble form in the solvent used.¹⁴² Anionic species can also be separated from others in solution by precipitation with cations. The commonly used anions in metal cation precipitation are chloride (Cl^-), bromide (Br^-), sulphate (SO_4^{2-}), carbonate (CO_3^{2-}), sulphide (S^{2-}), chromate ($\text{Cr}_2\text{O}_4^{2-}$), phosphate (PO_4^{3-}) and hydroxide (OH^-).¹⁹⁴ Advantages of precipitation include the simplicity and effectiveness of separation

¹⁹³ Precipitation reactions. [Accessed 03-10-2018]. Available at: [https://chem.libretexts.org/Textbook_Maps/Inorganic_Chemistry/Supplemental_Modules_\(Inorganic_Chemistry\)/Descriptive_Chemistry/Main_Group_Reactions/Reactions_in_Aqueous_Solutions/Precipitation_Reactions](https://chem.libretexts.org/Textbook_Maps/Inorganic_Chemistry/Supplemental_Modules_(Inorganic_Chemistry)/Descriptive_Chemistry/Main_Group_Reactions/Reactions_in_Aqueous_Solutions/Precipitation_Reactions)

¹⁹⁴ Chemical separation by precipitation. [Accessed 24-06-2018]. Available at: <http://www.science.uwaterloo.ca/~cchieh/cact/c123/separatn.html>

using this technique. Additionally, the selectivity is relatively high as certain target ions can be precipitated in the presence of others by paying attention to solubility rules. Disadvantages of the technique include the need for large amounts of precipitant, depending on the stoichiometry of the reaction.¹⁹⁵

4.4.3 LEACHING

Elemental recovery does not always require complete sample dissolution. In fact, it is sometimes very convenient to use a method that only achieves the dissolution and recovery of a certain element via the selective leaching or dissolution of target elements from the solid sample and in the process, reduce the number of separation steps. Leaching is the process of extracting a substance from a solid material which has come into contact with a liquid¹⁹⁶ and transfer an element of interest from naturally occurring ore into an aqueous phase. The solution which comes into contact with the solid sample is called the leach solution. It is important that the other components of the solid are insoluble in the leach solution to obtain a high purity metal ultimately. The resultant solution of leaching is called the leach liquor. A typical example is gold cyanide solution in gold recovery.¹⁹⁷

4.4.4 ION EXCHANGE CHROMATOGRAPHY

Ion-exchange chromatography (IEC) is a chromatographic process which separates ions and polar molecules in solutions according to their affinity to active sites on an ion-exchange resin.¹⁹⁸ The resin is an insoluble substance which contains loosely held ions and which can readily exchange with ions in a solution with which it makes contact. The resin is referred to as the stationary phase while the solution containing

¹⁹⁵ Chemical precipitation. [Accessed 25-06-2018]. Available at:

<https://emis.vito.be/en/techniekfiche/chemical-precipitation>

¹⁹⁶ A. Farooq. Leaching process (solid-liquid extraction). [Accessed 25-06-2018]. Available at:

<https://www.slideshare.net/asimfarooq31/leaching-process-solidliquid-extraction>

¹⁹⁷ D. S. Smit, F. B. Waanders. (2001). The leaching behavior of a Ni-Cu-Co sulphide ore in an oxidative pressure acid medium, M.Eng dissertation, University of Potchefstroom, pp.7-8

¹⁹⁸ J. Weiss. (2016). Handbook of ion chromatography, 4th ed., Germany, *Wiley-VCH Verlag GmbH & Co. KGaA*, p.30

the matrix of ions is the mobile phase. Ion-exchange chromatography is divided into two broad categories namely cation exchange chromatography and anion exchange chromatography. In cation exchange chromatography, the cations in the solution exchange with, or replace the loosely bonded cations on the resins and attach themselves to negatively charged sites which are part of the insoluble resin or stationary phase.

On the other hand, anion exchange chromatography entails the binding of anions onto positively charged sites in the stationary phase.¹⁹⁹ Synthetic ion-exchange resins are usually polymers, of high molecular mass, that contain vast amounts of an ionic functional group originating from the monomers which were used to synthesise it. Anion-exchange resins have basic or alkaline groups while cation-exchange resins contain acidic groups. Strong cation-exchange resins usually contain sulphonic acid groups ($-\text{SO}_3^-\text{H}^+$) and have a wider pH range for their applications compared to weak cation-exchangers, which contain the carboxylic acid group ($-\text{COOH}$). The structures of a strong acid polystyrene cation exchange resin with sulphonic groups and a strong base anion exchange resin with quaternary amine groups are depicted in **Figure 4.6a** and **Figure 4.6b** respectively.

¹⁹⁹ F. Rouessac, A. Rouessac. (2007). Chemical analysis: modern instrumentation methods and techniques, 2nd ed., West Sussex, England, *John Wiley & Sons, Ltd.*, p.96

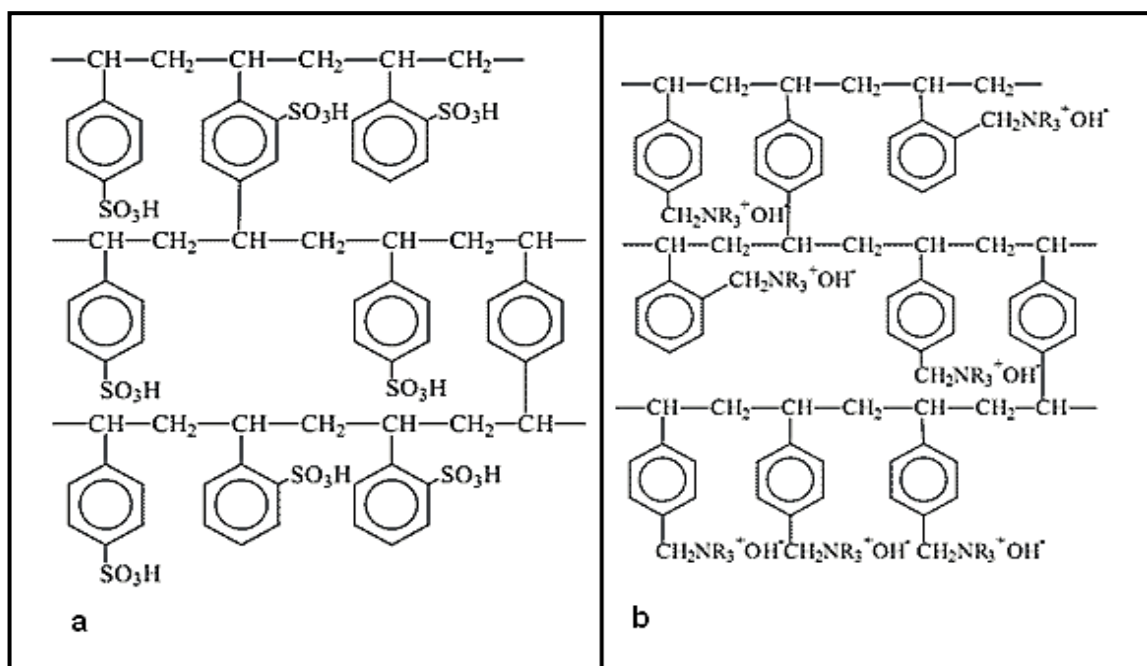
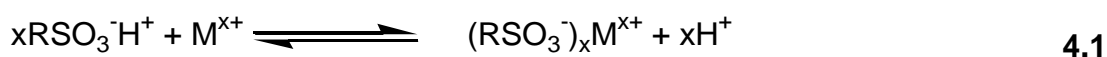
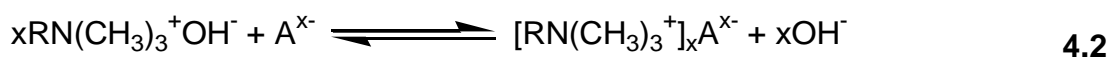


Figure 4.6: Ion exchange resins: a) A strong acid sulphonated polystyrene cation exchange resin, b) A strong base quaternary amine anion exchange resin²⁰⁰

The exchange is illustrated in **Equation 4.1** where M^{x+} denotes a cation and R denotes part of the molecule of the resin which is attached to one sulphonic acid group.



On the other hand, strong base anion exchangers usually contain quaternary amine groups $[\text{N}(\text{CH}_3)_3^+\text{OH}^-]$ whereas weak base anion exchangers contain secondary or tertiary amines. A strong base anion exchanger interacts with an anion (A^{x-}) as illustrated in **Equation 4.2**.



²⁰⁰ How ion exchange resins work. [Accessed 06-11-2018]. Available at: <http://www.ccdpy.com/ENLCAHIXRW.html>

The advantages of IEC include its high capacity of handling samples, relatively low cost compared to other liquid chromatographic techniques, the ease of scaling, the high resolution ability and the possible regeneration of the resin.²⁰¹ The process generally takes place in a minimum of five steps, as illustrated in **Figure 4.7**, namely loading of eluent, sample introduction, separation of sample's constituents, elution of analyte A and elution of analyte B. The eluent first displaces the anions which are bound to the resin (stationary phase) and covers the surface of the resin. The sample, which contains many ions including ions of interest A and B, is introduced into the column to form a mix with the mobile phase.²⁰² More of the eluent is added, facilitating the downward flow (gravitation) of the constituents of the sample at different rates due to their difference in affinity and strength to the active site and thus separating them. The ions A and B adhere to the surfaces of the resin and are later displaced by the eluent. Given that the ion A is displaced first, it is eluted first and may be collected separately. In the same manner, the ion B may be collected at a later stage or time individually as it is eluted from the column.²⁰³

²⁰¹ P. M. Cummins, O. Dowling, B. F. O'Connor. (2011). "Ion-exchange chromatography: basic principles and application to the partial purification of soluble mammalian prolyl oligopeptidase", *Methods in molecular biology*, 681, pp.215-228

²⁰² T. Wenzel. Basic principles of ion chromatography. [Accessed 14-04-2018]. Available at: https://chem.libretexts.org/Core/Analytical_Chemistry/Analytical_Sciences_Digital_Library/JASDL/Courseware/Separation_Science/07_Specialty_Topics/Ion-exchange_Chromatography/03_Basic_Principles_of_Ion_Chromatography

²⁰³ Y. M. Moustafa, R. E. Morsi. (2013). Ion exchange chromatography - an overview, Egyptian petroleum research institute (EPRI), pp.3-5

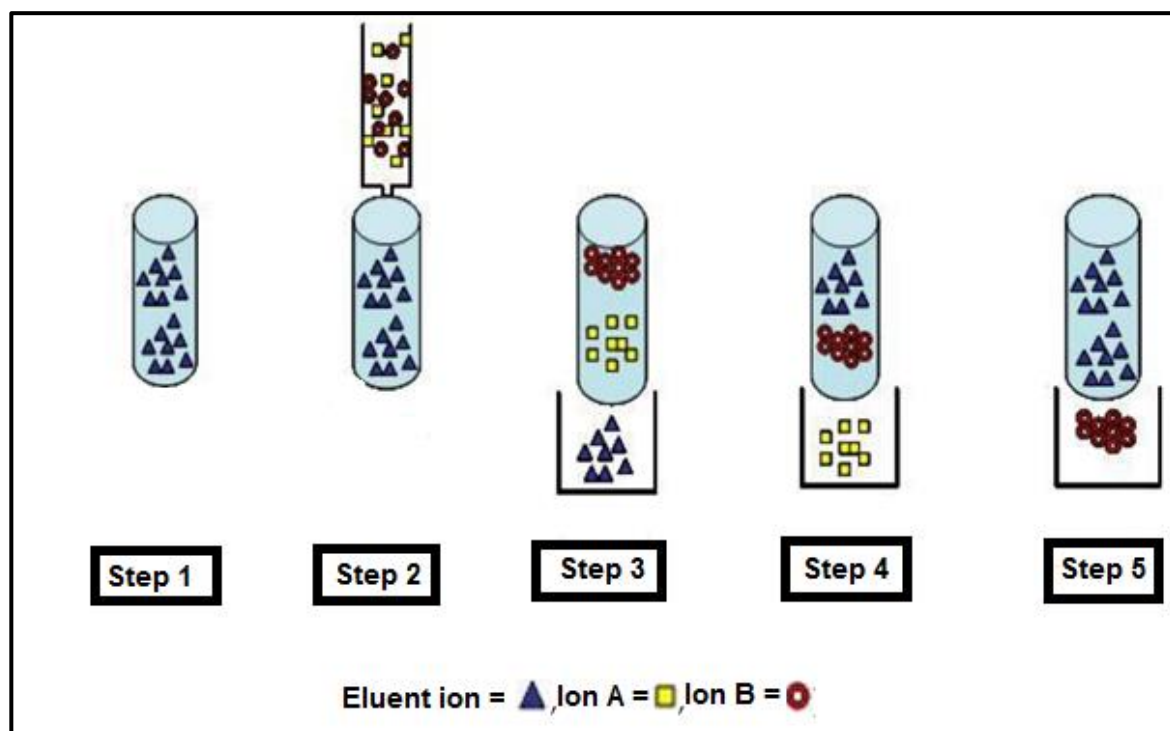


Figure 4.7: A schematic diagram for the processes in IEC ²⁰³

4.4.5 SOLVENT EXTRACTION

Many organic and inorganic solutes such as metal complexes distribute themselves between two immiscible liquid phases which are in contact with each other. The distribution between these two solvents is the result of the difference in solution solubility of the metal or elemental species which is used to separate chemical species successfully.²⁰⁴ The solubility differences between the different elements in solution is created by the addition of reagents such as acids, anions or complexing agents to selectively react with one of the elements in solution which changes its chemical and physical nature and thereby increases its solubility in one of the solvents compared to the other. A classic way to induce this difference is the addition of chelating agents to a metal ion aqueous mixture which ideally converts some of the metal ions into a neutral organometallic compound. The newly formed organometallic compound obtains more organic-type properties during this reaction,

²⁰⁴ H. F. Walton. (1964). Principles and methods of chemical analysis, 2nd ed., Englewood Cliffs, Prentice-Hall, p.179

thus reducing its solubility in the aqueous solution and increasing its solubility in immiscible organic solvents such as xylene, hexane and octanol.

In practice, the mixture containing the different elements is shaken vigorously in a separating funnel to maximise the contact between the two liquids, although no chemical reaction takes place between the two solvents. The solvents are then allowed to separate again. This method of separation is termed solvent extraction (also known as liquid-liquid extraction and partitioning). Two types of liquids are generally used, namely an aqueous solution and organic solvents.

A simplified model is used to describe the process. A solute containing a chemical species A is initially dissolved in one of the solvents, usually water. Upon the establishment of contact between the two solvents, A distributes between the two solvents until a point of equilibrium is reached. This means that a portion of the solute (A) moves from the aqueous phase into the organic phase as it is illustrated in **Equation 4.3**.²⁰⁵ The process is illustrated in **Figure 4.8**, showing the distribution process of the solute, initially in the aqueous phase, between the aqueous and organic phases. The organic solvent is usually the top layer due to its lower density. The continuous phase is an emulsion which forms after vigorous shaking. After phase separation, the solute is distributed between the two phases.



²⁰⁵ J.Rydberg, G. R. Choppin, C. Musikas, T. Sekine, M. Cox. (2004). Solvent extraction principles and extraction, 2nd ed. *Taylor & Francis Group, LLC*, p.1

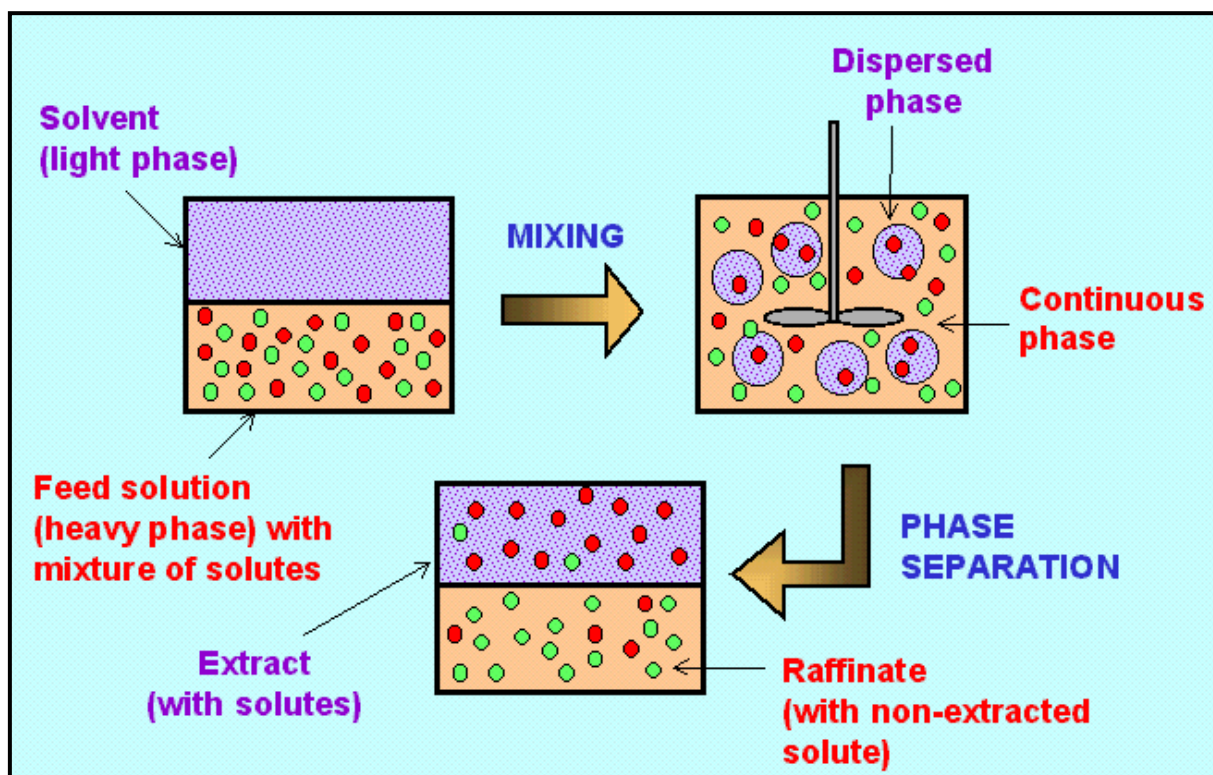


Figure 4.8: A schematic presentation of the solvent extraction process²⁰⁶

At the equilibrium point, the solute has a concentration $[A]_{\text{aq}}$ in the aqueous phase and $[A]_{\text{org}}$ in the organic phase, thus giving a distribution ratio (or distribution coefficient) as shown in **Equation 4.4**.²⁰⁷ At the equilibrium point, the rates at which molecules of A move from one solvent to the other are equal, thus giving no net exchange.

$$K_D = \frac{[A]_{\text{org}}}{[A]_{\text{aq}}} \quad 4.4$$

The two solutions can be separated easily when extraction takes place in a separating funnel, since most organic solvents are less dense than water and they generally float to the top of the mixture. Although the opposite is true for some

²⁰⁶ Liquid-liquid equilibria. [Accessed 26-06-2017]. Available at:

http://www.separationprocesses.com/Extraction/SE_Ch01.htm

²⁰⁷ J. Rydberg, M. Cox, C. Musikas, G. R. Choppin. (2004). Solvent extraction principles and practice, 2nd ed., Marcel Dekker, Inc., p.1

solvents, the general conventional rule is that the concentration of the solute in the organic phase ($[A]_{\text{org}}$) should always be the numerator. The amount of solute which is left in the aqueous layer after x extractions (n_x) can be calculated for a known K_d by use of **Equation 4.5**²⁰⁸ where n_0 denotes the initial amount of solute in the aqueous phase and V_{aq} and V_{org} are the volumes of the aqueous and organic phases respectively.

$$n_x = \left[\frac{V_{\text{aq}}}{(V_{\text{org}} K_D + V_{\text{aq}})} \right]^x n_0 \quad 4.5$$

In most cases, the solute exists in a number of chemical forms. The concentrations of the different species can be determined experimentally and these give rise to the distribution ratio, D . This is the ratio of the total concentration of all species of the solute in the organic phase to its total concentration in the aqueous phase (**Equation 4.6**²⁰⁹).

$$D = \frac{([A]_{\text{org}})_T}{([A]_{\text{aq}})_T} \quad 4.6$$

The success of the process may be determined by the extent of extraction (% E), the amount of solute in the organic phase as a percentage of the total amount of solute (**Equation 4.7**).

$$\%E = \frac{(V_{\text{org}} [A]_{\text{org}})}{(V_{\text{org}} [A]_{\text{org}} + V_{\text{aq}} [A]_{\text{aq}})} \quad 4.7$$

The distribution ratio can be related to the extent of extraction by substitution of **Equation 4.6** into **Equation 4.7** to give **Equation 4.8**.

²⁰⁸ D. A. Skoog, D. M. West, F. J. Holler, S. R. Crouch. (2004). Fundamentals of analytical chemistry, 8th ed., Brooks/Cole, Cengage learning, p.913

²⁰⁹ S. M. Khopkar. (1998). Basic concepts of analytical chemistry, 2nd ed., New Delhi, New age international (P) ltd. publishers, p.91

$$\%E = \frac{100D}{(D + \frac{V_{aq}}{V_{org}})} \quad 4.8$$

Numerous chelating agents (multi-dentate ligands) are usually weak acids that form neutral complexes, which have high solubility in organic solvents, with metals. The chelates formed are almost water-insoluble and the chelating agents are more soluble in organic solvents than they are in water. This makes it easy for the metal chelates to be extracted into the organic layer and therefore favours the separation process. **Figure 4.9** illustrates the mechanism of the extraction of a metal ion (M^{n+}) from the aqueous layer into the organic layer using the weak acid (HR).

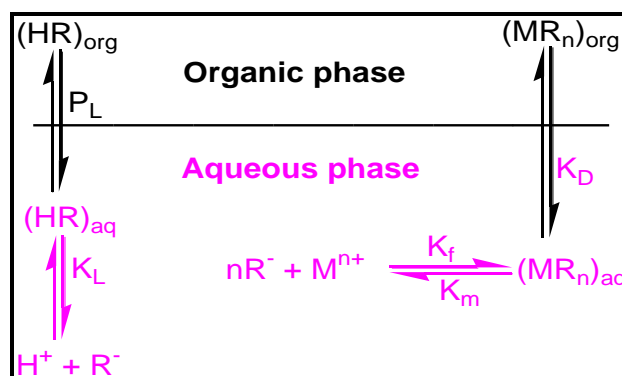


Figure 4.9: The reactions involved in the extraction of a metal ion²¹⁰

The weak acid (HR) distributed between the aqueous and organic phases, giving rise to P_L , the distribution constant of the chelating agent between the two phases.



$$P_L = \frac{[HR]_{org}}{[HR]_{aq}} \quad 4.10$$

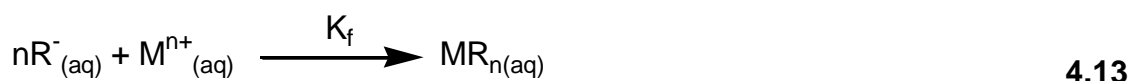
²¹⁰ M. Nete. (2013). "Separation and purification of niobium and tantalum from synthetic and natural compounds" Ph. D. thesis, University of the Free State, Bloemfontein, pp.69-71

The chelating agent dissociates in the aqueous phase to yield protons and R^- ions, giving rise to the dissociation constant to the chelating agent, K_L .



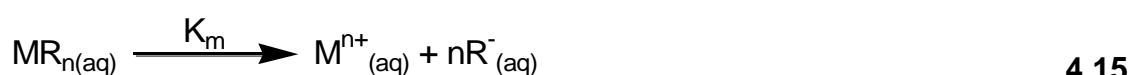
$$K_L = \frac{[H^+]_{aq}[R^-]_{aq}}{[HR]_{aq}} \quad 4.12$$

The anion (R^-) yielded by the dissociation reacts with the metal ion (M^{n+}) to form the metal chelate, giving rise to the formation constant.



$$K_f = \frac{[MR_n]_{aq}}{[M^{n+}][R^-]_{aq}^n} \quad 4.14$$

The reverse reaction occurs to dissociate the metal chelate, liberating the metal ion in solution and gives rise to K_m , the dissociation constant of the chelate.



$$K_m = \frac{[M^{n+}]_{aq}[R^-]_{aq}^n}{[MR_n]_{aq}} \quad 4.16$$

The metal chelate is then extracted into the organic phase.



$$K_D = \frac{[MR_n]_{org}}{[MR_n]_{aq}} \quad 4.18$$

Following these reactions which are involved in the metal extraction mechanism, the distribution ratio of the metal ion is a combination of the equilibrium constants involved.

$$D = \frac{K_D K_L^n}{K_m P_L^n} \quad 4.19$$

The advantage of the distribution ratio developed in **Equation 4.19** is that it allows the researcher to study each individual step of the extraction process in detail. The process develops a thorough understanding of the individual steps in the process and identifies reaction limiting steps which allows for interventions or control to improve the extraction.

The advantages of solvent extraction include the time efficiency in obtaining a quantitative separation, the ability to succeed in high quantities as well as in trace amounts and its profitability when applied in the recovery of metals.²¹¹ The drawbacks include the need for numerous steps for optimum extraction, use of large volumes of organic solvents which are expensive to recycle and the need for removal of the traces of the eluent before evaporation of the organic solvent.²¹²

4.5 ELECTROWINNING

Electrowinning is an electrolytic process in which an external voltage is applied to a chemical solution to selectively recover a metal from the electrolyte solution by its deposition onto a cathode.²¹³ The metal ions are reduced by the electrons supplied

²¹¹ G. L. D. Krupadanam, D. V. Prasad, K. V. Rao, K. L. N. Reddy, C. Sudhakar. (2004). Analytical chemistry, *Orient Longman private limited*, p.46

²¹² F. F. Cantwell, M. Losier. (2002). "Liquid-liquid extraction", *Comprehensive analytical chemistry*, Elsevier B. V., p.300

²¹³ M. L. Free, The minerals, metals & materials society. (2013). *Hydrometallurgy: fundamentals and applications*, 1st ed., *John Wiley & sons, Inc.*, p.218

by the external current to produce the solid metal²¹⁴ during this process which is extensively employed in the industry to produce metals such as copper, zinc, silver, cadmium and gold. As metals deposit on to the cathode and build up on it, the rate of deposition decreases until an insufficient level is reached. At this point, the cathode may safely be removed from the electrolytic cell.²¹⁵ An electrowinning unit (**Figure 4.10**) has three main components namely an electrolytic cell, a rectifier and a pump. An electrolytic cell consists of a tank made of non-conducting plastic material, in which cathodes and anodes are placed in an alternating order, connected to bus bars which provide the electrical potential. The circulation of the liquid within the cell may be improved by components which include air spargers and a flow disperser.²¹⁶

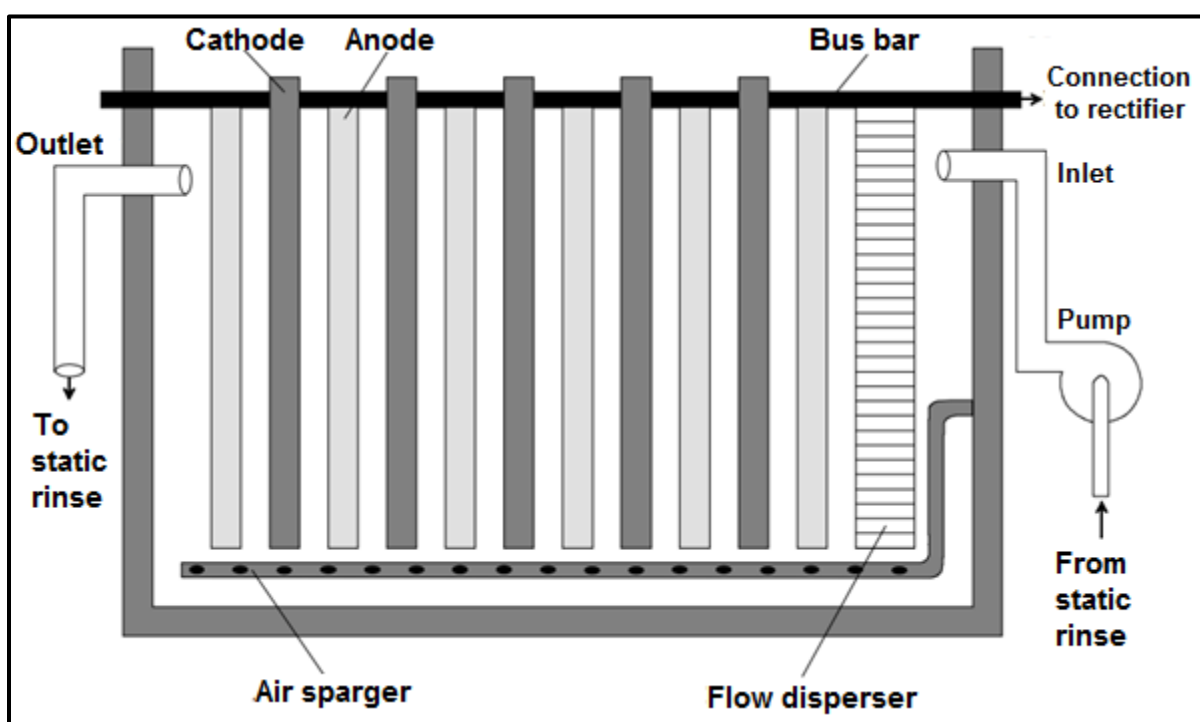


Figure 4.10: Cross-section of an industrial electrowinning unit²¹⁶

²¹⁴ N. T. Beukes, J. Badenhorst. (2009). "Copper electrowinning: theoretical and practical design", *Hydrometallurgy conference 2009, South Africa*, pp.213-240

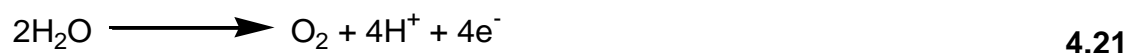
²¹⁵ L. Smith, J. Means. (1994). *Recycling and reuse of material found on superfund sites*, Washington, DC, Center for environmental research information, p.44

²¹⁶ Metal recovery and wastewater reduction using electrowinning. [Accessed 28-05-2018]. Available at: <http://sterc.org/pdfs2/metal-ewin.pdf>

Normally, the anode is manufactured from lead through which the electric current enters and bears a positive charge while the cathode is associated with the negative pole. The applied direct current passes through the anode and exits through the cathode. The negative charge on the cathode's surface attracts the positive ions in the electrolyte solution and they move towards the cathode.²¹⁷ The electrons then react with the metal ions to reduce them (see **Equation 4.19**²¹⁸). M is the metal in consideration while n is the number of electrons required to reduce it to the zero oxidation state.



The oxidation of water (see **Equation 4.21**²¹⁸) to evolve oxygen is the most common anodic reaction in the electrowinning of metals from acidic electrolyte solutions. This reaction also produces acid.



Generally and among the base transition elements, zinc and copper are the most commonly electrowon metals. However, the technique can also be applied on other metals which include nickel, cobalt, chromium and manganese.²¹⁹ Modern techniques in electrowinning have been deduced by modification of the classical version. A typical example is the energy-efficient electrowinning process which uses magnetically-modified electrodes, which is used for base metal recovery from dilute

²¹⁷ G. C. Cushnie Jr. (2009). Pollution prevention and control technologies for plating operations, 2nd ed., *National center for manufacturing sciences*, p.177

²¹⁸ K. I. Popov, S. S. Djokic, B. N. Grgur. (2002). Fundamental aspects of electrometallurgy, 2nd ed., *Kluwer academic publishers*, p.175

²¹⁹ S. Schmachtel, M. Toiminen, K. Kontturi, O. Forsen, M. H. Barker. (2009). "New oxygen evolution anodes for metal electrowinning: MnO₂ composite electrodes", *Applied electrochemistry*, 39, pp.1835-1848

precious metal concentrates and the treatment of wastewaters which may contain toxic heavy metals such as cadmium and lead.²²⁰

Electrowinning has a main advantage of low cost as it removes metals without requirement of further processing.²¹⁵ In this technique, no additional waste is generated during the process. The limitations of the technique include its decreased efficiency at low concentrations of metals and not removing metals below acceptable limits for discharge. Additionally, the electrodes must be made of metals which do not easily react with acids which are usually used and this may increase the cost of operation.

4.6 CONCLUSION

The methods that have been discussed in this chapter can successfully be applied to the beneficiation of mine waste. Digestion by acids (acid leaching) may be applied on waste rock and on tailings and flux-fusion to dissolve the samples completely and liberate the valuable elemental content for beneficiation. Although fusion may pose negative matrix effects on the sample solution, the complete dissolution allows accurate quantification while acid-digestion may not get the total elemental content into the liquid phase. The ICP-OES is the best quantification technique compared to other techniques such as atomic absorption spectroscopy (AAS) and it owes this to the advantages as outlined in **Section 4.3.1**. The separation techniques which have been covered in this chapter can be applied well in the recovery of valuable metals from mine waste. Electrowinning can be used on waste as much as it is used in the recovery of metals in metallurgical processing. The challenge, however, is the complex matrix of the waste which can pose challenges on selectivity. This challenge

²²⁰ M. Coey, D. Fernandez., Energy efficient electrowinning and electrorefining using magnetically-modified electrodes. [Accessed 31-05-2018]. Available at:
<http://www.crann.tcd.ie/CRANN/media/CRANN/PDFs/Available%20Technologies/Energy-Efficient-Electrowinning-and-Electrorefining-Using-Magnetically-Modified-Electrodes.pdf>

can be overcome by performing the techniques at suitable conditions for the target element.

5 SAMPLE COLLECTION, PREPARATION AND QUANTIFICATION

5.1 INTRODUCTION

The primary aim of this study is to determine the elemental content and value of gold mine waste material in the Free State. The first objective (this chapter) is to determine the types and quantities of elements in the different waste products at the waste sites, while the second objective (**Chapter 6**) will explore different chemical processes, to isolate and recover elements deemed valuable from the waste material.

Gold mine waste dumps in the Welkom/Virginia area in the Northern Free State, in South Africa, were selected for this study. The first traces of gold were discovered in 1933 during drilling activities on the farm 'Aandenk' (place where the town Allanridge is currently situated).²²¹ Very soon afterwards (1938), gold was discovered in close proximity on the farms of St. Helena and Uitsig.²²² After deepening the borehole at 'Aandenk' with another 120 m in 1945, the Anglo-American corporation reached the Basal reef which yielded payable gold deposits and intensive gold mining started shortly after this discovery.²²³ Current estimates indicate that mining activities from the Welkom area (**Figure 5.1**) produced approximately 21% of the world's gold sales to date.

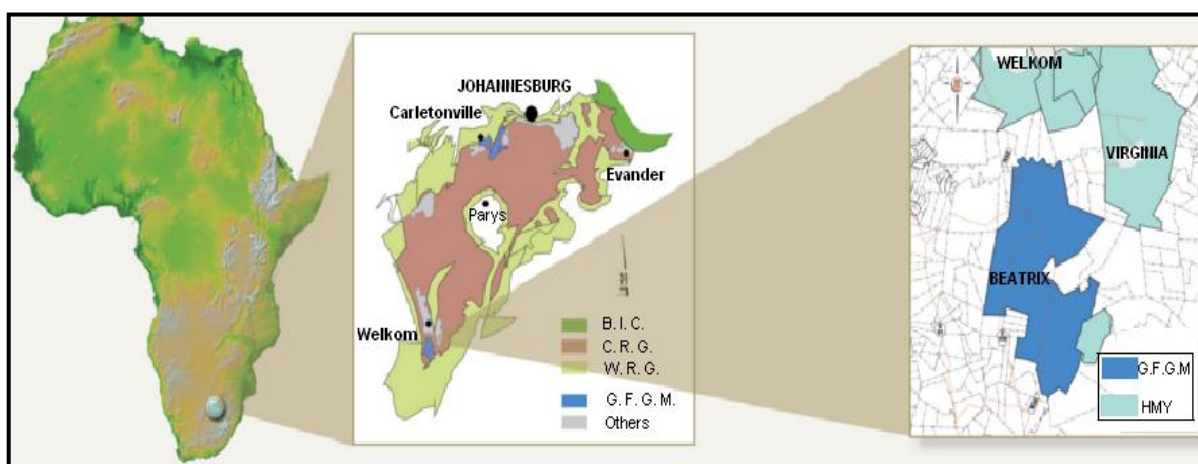
²²¹ M. B. van den Heever. (2008). A sedimentological investigation of B-reef at Masimong 5 shaft. M. Sc. Dissertation, University of the Free State, Bloemfontein, p.3

²²² R. Edwards, K. Atkinson. (1986). Ore deposit geology and its influence on mineral exploration, 1st ed., *Chapman and Hall Ltd.*, p.209

²²³ Prospecting bore-hole, Aandenk, Odendaalsrus District. [Accessed 29-11-2018], Available at: <https://www.sahra.org.za/sahris/sites/923280001>

Decades of gold mining activities left the Welkom/Virginia area (also in the Witwatersrand) littered with huge and ugly mine waste dump sites. Some initiatives are currently being undertaken in the country to re-process the slime dumps for gold recovery. In some cases, these yield approximately 0.45 g of gold for every tonne of waste material reprocessed.²²⁴ This study, however, represents an investigation into the presence of all other elements found in the waste materials that have already been mined and brought to the surface.

Three different types of waste products have been identified from these waste sites. The first, which is called waste rock, is obtained from the excavation activities to reach the gold-bearing ore bodies. The second kind of waste comprises the slime dumps (tailings). This waste is the product obtained after the chemical processing of the gold-bearing ores has taken place. The third kind waste product identified is the different water bodies in close proximity of the slime dumps. This waste type was also investigated for elemental content in this study.



B.I.C= Bushveld igneous complex, C. R. G= Central rand group, W.R.G.= West rand group, G. F. G. M.= Gold fields gold mines, HMY= Harmony

Figure 5.1: Gold deposits in Welkom indicating mining companies²²⁵

²²⁴ Welkom. [Accessed 29-11-2018]. Available at: <https://en.wikipedia.org/wiki/Welkom>

²²⁵ Mineral resources and mineral reserves overview 2009. [Accessed 25-11-2018]. Available at: https://www.goldfields.com/reports/rr_2009/tech_beatrix.php

This part of the study describes the sampling of the solid waste (waste rock and tailings) and water samples, the dissolution of solid samples, the identification and the quantification of the elements that are present in the waste with ICP-OES.

5.2 GENERAL EXPERIMENTAL METHODOLOGY, CONDITIONS AND APPARATUS

5.2.1 COLLECTION OF SAMPLES

All three forms of waste material (waste rock, tailings and mine water from a ditch) were collected from mine dumps in the vicinity of Welkom and Virginia, in the Free State province of South Africa.

5.2.1.1 *Sampling of waste rock*

Samples were collected from six mine dumps whose coordinates are shown in **Table 5.1**. From each dump of waste-rock, five samples were randomly collected at different points. These were selected to include waste with different particle sizes and surface colours. The samples have been labelled in a way that the first letter and subscript indicate the dump number and the second letter together with its subscript indicate the sample number from the certain site.

Table 5.1: The location coordinates of the mine waste rock dumps

| Dump number | Coordinates | |
|-------------|-------------------|-------------------|
| | S | E |
| 1 | 27° 46' 52.0487" | 26° 38' 42.8941" |
| 2 | 27° 49' 27.49441" | 26° 38' 33.0219" |
| 3 | 27° 50' 49.61601" | 26° 40' 18.92479" |
| 4 | 27° 51' 49.61952" | 26° 43' 11.91624" |
| 5 | 27° 54' 10.87267" | 26° 42' 9.809557" |
| 6 | 27° 58' 0.954988" | 26° 41' 43.85387" |

From dump 1, the following samples were collected: $D_1S_{1coarse}$, D_1S_{1fine} , $D_1S_{2coarse}$, D_1S_{2fine} and D_1S_3 . Samples $D_1S_{1coarse}$ and D_1S_{1fine} were collected at the same point, but differ in terms of particle size. The latter represented smaller particles. The same applies for $D_1S_{2coarse}$ and D_1S_{2fine} , both having a yellow surface. D_1S_3 was collected at a third point, the farthest from the first point of collection, and had a brown surface. From dump 2, the following samples were collected: D_2S_1 , D_2S_2 , D_2S_3 , D_2S_4 and D_2S_5 . D_2S_1 possessed a green surface and was collected from the first point, closest to the point of entrance. D_2S_2 was taken from a second point, followed by D_2S_3 collected from a third point. The last two samples, D_2S_4 and D_2S_5 were collected at two points but both had yellowish surfaces. The names of the specific mines are withheld to protect them of any incriminating results which may arise from this study.

The samples were all milled into fine powder. The five samples per dump were combined by manually homogenising equal masses of each sample in order to investigate the average characteristics of the respective dumps. For example, the samples D_2S_1 to D_2S_5 were combined by manual homogenisation of 10 g of each to form a combined sample D_2 which represents the entire dump. All samples were then transferred into plastic bottle containers.

5.2.1.2 Sampling of tailings

Tailings samples were collected in May 2017 from three slime dumps located around Welkom. The sampling was carried out at different elevations on the slime dumps as indicated in **Figure 5.2** and each layer was about 3 m high. Eleven samples, in total, were collected (three samples from dump B, four samples from dump T and four samples from dump S) at three different dumps. The first sample at each dump was collected from the ground level (base of the dump) while the second sample was collected from the first layer of the dump (0 to 3 m from the ground) and the third sample was collected from the second layer of the dump (3 to 6 m from the ground). The dump site labelled S was an exception to the rule since only one layer was observed and sampled.

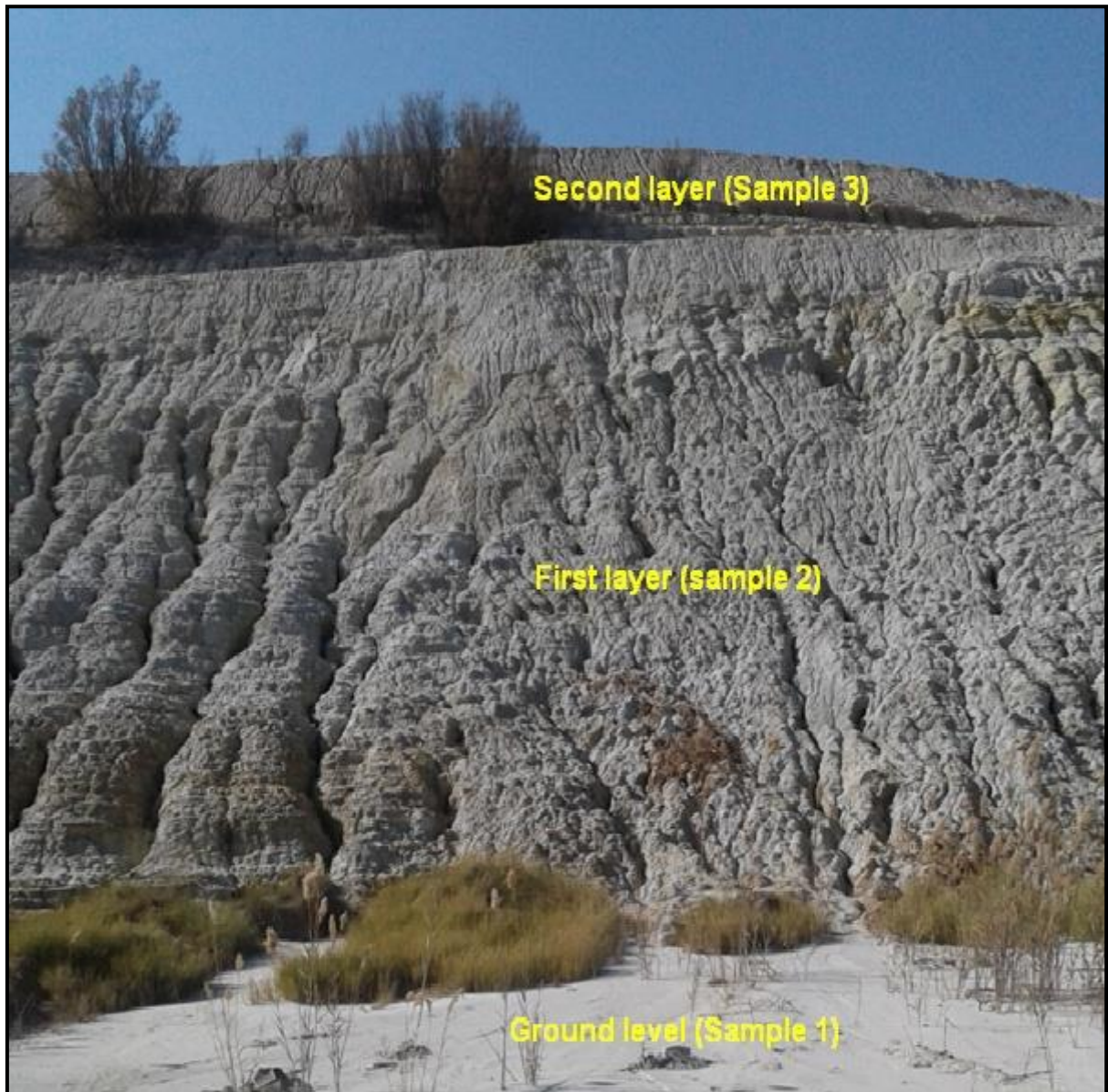


Figure 5.2: A dump of tailings with different layers, showing the different levels on which samples were collected

The fourth sample at dump site T was collected from a dried streambed while the third and fourth samples from dump S were collected at yellowish patches observed on a drive-way (**Figure 5.3**) beside the slime dump. The driveway was located at a ground level on the opposite side of the ditch. **Table 5.2** is a summary of the samples of tailings and the respective descriptions.



Figure 5.3: Drive-way soil with yellowish patches

Table 5.2: The samples of tailings and their descriptions

| Description | S | T | B |
|-----------------------------|---------------------------------|----------------|----------------|
| Ground level | S ₁ | T ₁ | B ₁ |
| First layer | S ₂ | T ₂ | B ₂ |
| Second layer | - | T ₃ | B ₃ |
| Dry streambed sediments | - | T ₄ | |
| Yellowish patch on driveway | S ₃ , S ₄ | | |

5.2.1.3 Sampling of water bodies

Water samples were collected from the ditches surrounding the tailings dumps at sites B and S. These include S_{w1} and B_{w1} (May 2017) which were both collected in the form of water samples only. Further samples, B_{w2} and B_{w3} (August 2017) were collected together from the ditch surrounding dump B but these samples consisted of both water and streambed sediments. Samples B_{w4} and B_{w5} were collected from the ditch surrounding dump B in November 2017. B_{w4} comprised water and streambed

sediments while B_{w5} comprised drainage coming from a pipe projecting from the dump. The pH measurements were carried out on field and HNO₃ was added to prevent the possible precipitation of the elements in solution. **Table 5.3** summarises the water samples and their pH.

Table 5.3: The water samples collected and their pH values

| Sample | Description | pH |
|-----------------|---------------------|------|
| B _{w1} | Water | 3.54 |
| S _{w1} | Water | 6.58 |
| B _{w2} | Water and sediments | 6.94 |
| B _{w3} | Water and sediments | 6.81 |
| B _{w4} | Water and sediments | 7.29 |
| B _{w5} | Drainage from pipe | 6.85 |

5.2.2 GENERAL EXPERIMENTAL CONDITIONS AND APPARATUS

5.2.2.1 *Ultra-pure water system*

Ultra-pure water of conductivity 0.00 mS/cm was used throughout the study to prepare sample solutions and standard solutions. The water was prepared by reverse osmosis using a purification system supplied by AJD Traders.

5.2.2.2 *Electronic Balance*

A Shimadzu AW 320 electronic balance was used for all weighing operations of samples, and reagents.

5.2.2.3 *Magnetic stirrer*

A Heidolph MR Hei-Tec magnetic stirrer with a heating plate of diameter 145 mm and temperature range of 0 to 300 °C was used for stirring of melt-acid mixtures obtained from the flux-fusion studies. The maximum stirring rate capability of the stirrer is 1400 rpm.

5.2.2.4 Glassware

Schott Duran (Grade A) volumetric flasks of volumes 10.0 mL, 25.0 mL and 100.0 mL were used for sample dissolution, standard solution preparation and sample dilution operations. Glassco beakers made of borosilicate glass were also used. A 10 mL glass pipette was used to transfer aliquots of acid (to ensure matrix matching).

5.2.2.5 ICP-OES

The Shimadzu sequential plasma emission spectrometer ICPS-7510 was used for qualitative and quantitative analyses of the mine waste solutions after preparation and after separation attempts. The operating conditions are summarised in **Table 5.4**.

Table 5.4: The operating conditions used in elemental analyses with ICP-OES

| Parameter/Feature | Condition/Feature type |
|----------------------|------------------------|
| RF power | 1.2 kW |
| Coolant gas flow | 14.0 L/min |
| Plasma gas flow | 1.2 L/min |
| Carrier gas flow | 0.5 L/min |
| Sample uptake method | Peristaltic pump |
| Spray chamber | Glass cyclonic |
| Type of nebuliser | Concentric tube |

5.2.2.6 SEM-EDS

A Tescan VEGA3 SEM with an Oxford X MaxN EDS operating with SEM electronics was also used for quantitative analysis of tailings.

5.2.2.7 Ovens

A Thermo Scientific Thermolyne muffle furnace, with a heating capacity of 1100 °C, was used for the flux fusion dissolutions. The Memmert oven was used to dry tailings with some moisture which operates at an adjustable temperature range of 50 – 300 °C.

5.2.2.8 Micropipettes

The Gilson Pipetman P 10 mL single channel classic pipettes were used in sample preparation and dilution while a Boeco SP series (adjustable volume) 1000 μ L pipette was used for standard solution preparation.

5.2.3 REAGENTS

Commercially available reagents were used in their state of receipt. The information about the reagents is given in **Table 5.5**. The analytically pure reagents are safer to use in trace analyses.

Table 5.5: The purity and supplier information of reagents

| Chemical name | Formula | Purity (%) | Supplier |
|--|--|------------|---------------------------------|
| Nitric acid (TG) | HNO ₃ | 55 | Associated Chemical Enterprises |
| Nitric acid (AG) | HNO ₃ | 65 | |
| Sulphuric acid (AG) | H ₂ SO ₄ | 98 | |
| Orthophosphoric acid (AG) | H ₃ PO ₄ | 85 | |
| Hydrochloric acid (AG) | HCl | 32 | |
| Lithium tetraborate | Li ₂ B ₄ O ₇ | 99.5 | Claisse |
| Potassium Pyrosulphate | K ₂ S ₂ O ₇ | 97.5 | Saarchem |
| Potassium fluoride | KF | 98 | |
| Ammonium bifluoride | NH ₄ HF ₂ | - | Merck |
| Potassium bifluoride | KHF ₂ | | - |
| Sodium phosphate monobasic monohydrate | NaH ₂ PO ₄ •H ₂ O | ≥98 | Sigma-Aldrich |
| Sodium phosphate dibasic | Na ₂ HPO ₄ | 99 | |

AG – Analytically pure grade, TG – Technical laboratory grade, - = information not provided

5.2.3.1 ICP Standards

The ICP multi-element standard (containing 23 elements including Cd, Cu, Fe, Co, Cr, Mn and Pb in HNO₃) as well as a Pt standard in HCl (7% v/v, 1000 mg/L) and a sulphur standard (H₂SO₄, 1000 mg/L) in H₂O were purchased from Merck. Inorganic ventures supplied standard solutions for Ti in HNO₃ (2% v/v, 1000 mg/L) and Th in HNO₃ (5% v/v, 1000 mg/L). A U standard in HNO₃ (5% v/v, 1000 mg/L) was purchased from Ultraspec while Hg standard in HNO₃ (12% w/w 1000 mg/L) and Zr in HF (1000 mg/L) were purchased from Fluka and Inorganic ventures respectively.

5.2.3.2 Cleaning of apparatus

All glassware and stirring magnets were soaked using aqua-regia, prepared with 32% HCl and 55% HNO₃ solutions, for 12 to 24 hours and rinsed three times with ultra-pure water prior to their use.

5.2.4 ICP-OES CALIBRATION

5.2.4.1 Preparation of calibration standard solutions and curves

The standard solutions outlined in **Section 5.2.3.1** were used to prepare calibration standard solutions of concentrations 1, 3, 5, 7 and 10 ppm with respect to the different elements. A 1000 mg/L P stock standard solution was prepared with 85% phosphoric acid. The appropriate volumes (100, 300, 500, 700 and 1000 µL) of the 1000 mg/L standard solutions were quantitatively transferred into previously cleaned 100.0 mL volumetric flasks using a micropipette. To prepare different sets of standards, different acids were used namely 65% HNO₃ and 85% H₃PO₄. The respective acids (10 mL) were added into the volumetric flasks containing the standards. The flasks were then filled with ultra-pure water while ensuring its homogenisation with shaking. The blank solutions (0.0 ppm) were prepared for background intensity corrections by transferring 10 mL of the respective acids into 100.0 mL volumetric flasks and filling to the mark with ultra-pure water. The standard solutions were then allowed to stabilise for at least 24 hours before analysis. The standard solutions used for the fused solid samples were spiked with a solution of

$\text{Li}_2\text{B}_4\text{O}_7$ in H_3PO_4 . The selected wavelengths used for the elemental analyses are given in **Table 5.6**.

Table 5.6: The analysed elements and their wavelengths

| Element | Wavelength (nm) |
|---------|-----------------|
| Pt | 224.552 |
| Ti | 337.280 |
| Th | 318.020 |
| U | 367.007 |
| S | 180.731 |
| Mn | 293.930 |
| Fe | 234.349 |
| Cu | 213.598 |
| Cd | 226.502 |
| Co | 236.379 |
| Zr | 357.247 |
| Cr | 284.325 |
| Al | 394.403 |
| Hg | 194.227 |
| As | 228.883 |
| Pb | 220.353 |
| P | 203.349 |

5.2.4.2 Detection and quantification limits

The calibration curves of the different analytes were used to calculate the limit of detection (LOD) and the limit of quantification (LOQ) for each analyte according to **Equation 5.1** and **Equation 5.2**. The gradients of the calibration curves (m) and the standard deviations of the blank solution (SD) (tenfold analysis) in two different acid matrices, namely phosphoric acid and nitric acid, were used in these calculations.

$$\text{LOD} = 3.3 \times \frac{\text{SD}}{m}$$

5.1

$$\text{LOQ} = 10 \times \text{LOD}$$

5.2

The calculated limits of detection and quantification in phosphoric and nitric acids are reported in **Table 5.7** and **Table 5.8** respectively.

Table 5.7: The limits of detection and quantification in H_3PO_4

| Element | Standard deviation | Slope (L/mg) | LOD (mg/L) | LOQ (mg/L) |
|---------|--------------------|--------------|------------|------------|
| Al | 0.001669 | 0.056 | 0.098352 | 0.983518 |
| S | 0.000111 | 0.005 | 0.07326 | 0.7326 |
| Ti | 0.001768 | 1.24 | 0.004705 | 0.047052 |
| Cr | 0.000417 | 0.125 | 0.011009 | 0.110088 |
| Mn | 0.001001 | 0.259 | 0.012754 | 0.127541 |
| Fe | 0.000617 | 0.082 | 0.02483 | 0.248305 |
| Cu | 0.001052 | 0.245 | 0.01417 | 0.141698 |
| Zr | 0.003014 | 0.532 | 0.018696 | 0.186959 |
| Pt | 0.000507 | 0.011 | 0.1521 | 1.521 |
| Th | 0.001617 | 0.086 | 0.062048 | 0.620477 |
| U | 0.001895 | 0.025 | 0.25014 | 2.5014 |

Table 5.8: The limits of detection and quantification in HNO₃

| Element | Standard deviation | Slope | LOD | LOQ |
|---------|--------------------|--------|----------|----------|
| S | 0.000176 | 0.005 | 0.116092 | 1.160924 |
| Ti | 0.011432 | 1.832 | 0.020592 | 0.205923 |
| Cr | 0.001951 | 0.156 | 0.041278 | 0.412775 |
| Mn | 0.003308 | 0.316 | 0.034548 | 0.345477 |
| Fe | 0.001498 | 0.098 | 0.050453 | 0.504531 |
| Co | 0.001248 | 0.075 | 0.054894 | 0.548939 |
| Cu | 0.001157 | 0.073 | 0.052323 | 0.523233 |
| As | 0.001145 | 0.271 | 0.013941 | 0.139406 |
| Cd | 0.001289 | 0.45 | 0.009452 | 0.094519 |
| Pt | 0.000499 | 0.012 | 0.137345 | 1.373447 |
| Hg | 0.000166 | 0.018 | 0.030504 | 0.305037 |
| Pb | 0.001078 | 0.028 | 0.127052 | 1.270524 |
| Th | 0.0015 | 0.112 | 0.04428 | 0.44283 |
| U | 0.002 | 0.0439 | 0.15024 | 1.5024 |
| P | 0.003294 | 0.004 | 0.099122 | 0.991217 |

The limits of detection for all the elements were found to be low for the elements except Th, U, Pt, S and Pb. The possible reasons for the higher detection limits are relatively large standard deviations of the blank solution's intensity or the low sensitivity (slope) of the instrument towards the above elements. Although this also raised the limits of quantification, the elements could still be detected at low concentrations. The limits of the metals were lower in the HNO₃ matrix than in the H₃PO₄ matrix.

5.2.5 DISSOLUTION AND QUANTIFICATION OF MINE WASTE SAMPLES

The next step in this study involved the dissolution of the collected solid waste samples (described in **Sections 5.2.1.1** and **5.2.1.2**).

5.2.5.1 Dissolution of waste rock by flux-fusion

5.2.5.1.1 Experimental

In an attempt to dissolve the waste rocks samples completely (for accurate chemical characterisation), several fluxes were used. The methods are summarised in **Table 5.9**.

The waste rock samples D₁ - D₆ were dissolved by fusion with different fluxes. In a platinum crucible, 1 g of the flux was mixed with accurately weighed sample (0.4999 - 0.5083 g) and manually homogenised. The mixture was heated in a muffle furnace at 1100 °C for 30 minutes. The crucible was then taken out of the furnace and allowed to cool on a marble bench top. The crucible was placed in a 100 mL beaker, followed by addition of dilute orthophosphoric acid (10 mL of 85% H₃PO₄ in 60 mL ultra-pure water). The beaker was then placed on a magnetic stirrer at about 80 °C for 20 minutes. The solution was allowed to cool and transferred quantitatively into a 100.0 mL volumetric flask. The flask was then filled to the mark with ultra-pure water. It was then allowed to stabilise for 24 hours. The solutions were analysed qualitatively and then quantitatively by ICP-OES.

Visual inspection indicated that lithium tetraborate was the most effective in the complete dissolution of the waste samples. However, the use of HCl and H₂SO₄ to dissolve the melt resulted in the precipitation of some metals as chlorides and sulphates respectively. Although complete dissolution was achieved with KF as fusion medium and subsequent H₂SO₄ dissolution, it was decided on safety concerns (potential HF formation and release) to stop this part of the study. Fusion with Na₂O₂ in a nickel crucible also showed promise. However, the melt and the resultant solution appeared black in the Ni crucible although upon heating, the solution turned clear. Nevertheless, this method was also abandoned to avoid any possible elemental contamination.

Table 5.9: Reagents and conditions used in flux fusion dissolution for waste rock samples

| Flux | Ratio | Temp. (°C) | Fusion Time(min) | Acid | Stirring Time | Result |
|--|-------|---------------|---------------------|--------------------------------|------------------|--------------------------------------|
| Li ₂ B ₄ O ₇ | 1:10 | 1100 | 30 | HCl | 1 week | Precipitate observed |
| Li ₂ B ₄ O ₇ | 1:10 | 1100 | 30 | H ₂ SO ₄ | 45 h | Precipitate observed |
| K ₂ S ₂ O ₇ | 1:10 | 800 | 30 | HCl dil | 1 h | Incomplete |
| NH ₄ HF ₂ | 1:10 | 225 | 30 | HCl dil | 1 h | Incomplete |
| KHF ₂ | 1:10 | 350 | | HCl dil | 1 h | Incomplete |
| KF | 1:10 | 950 | 30 | HCl | 30 h | Precipitate observed |
| KF | 1:10 | 950 | 30 | H ₂ SO ₄ | 4 h | Complete (Cloudy) +Δ→ Clear |
| Li ₂ B ₄ O ₇ | 1:10 | 1100 | 30 | HNO ₃ | 1 h | Incomplete |
| Na ₂ HPO ₄ / NaH ₂ PO ₄ •H ₂ O | | 800 | 30 | H ₃ PO ₄ | 1h | Incomplete |
| Na ₂ O ₂ | 1:10 | 800 | | HNO ₃ | 1 | Black in water +Δ → Clear |
| Li ₂ B ₄ O ₇ | 1:10 | 1100 | 30 | H ₃ PO ₄ | 1 | Complete |

Δ = Heat

5.2.5.1.2 Results and discussion

Table 5.10: The concentrations of elements in waste rock samples after $\text{Li}_2\text{B}_4\text{O}_7$ flux fusion

| Element | Concentration (mg/kg) | | | | | |
|---------|-----------------------|----------------|----------------|----------------|----------------|----------------|
| | D ₁ | D ₂ | D ₃ | D ₄ | D ₅ | D ₆ |
| Al | 5029(95) | 3754(50) | 3048(77) | 3264(449) | 2858(160) | 2513(97) |
| S | 1159(112) | 1497(52) | 987(270) | 725(97) | 587(68) | 709(89) |
| Ti | 1984(97) | 1161(139) | 1204(71) | 932(77) | 1068(30) | 1417(61) |
| Cr | 197(4) | 277(28) | 174(3) | 109.8(6.5) | 185(3) | 304(19) |
| Mn | 155(5) | 205(23) | 112(3) | 58.6(1.4) | 96(1) | 158(5) |
| Fe | 1626(40) | 1817(38) | 1100(5) | 978(48) | 995(23) | 2029(15) |
| Zr | 134(6) | 97(17) | 106.1(3.6) | 74.6(9.9) | 116(7) | 175(11) |
| Pt | 193(9) | 208(23) | 85(25) | 35.2(11.3) | 28(4) | 117(10) |
| Th | 71(3) | 96(7) | 0 | 0 | 0 | 31.6(5) |

() = Standard deviation

The $\text{Li}_2\text{B}_4\text{O}_7$ flux proved to be the most effective to dissolve the waste rock samples. However, a formation of white precipitate was observed when HCl and H_2SO_4 were used in dissolving the melt, pointing to the formation of insoluble chlorides and sulphates. The use of H_3PO_4 at an elevated temperature proved to be extremely effective to dissolve the melt without precipitate formation. The quantification of the samples was challenging due to the presence of high salt content originating from the alkali flux salts, as well as the high concentrations of some of the elements including Al, Fe and S in the waste rock samples. Large waste rock sample sizes were used in order to increase the concentrations of trace and ultra-trace elements for accurate quantification and identification purposes. This, however, compromised the precision of the concentrations of trace elements while the precision was acceptable (1.9% RSD) for the major elements since they were present in very high concentrations. The results further indicate that the waste rock was dominated by Al, Fe, Ti and S.

5.2.5.2 Investigation of the effect of particle size

5.2.5.2.1 Experimental

The next step in this study is to investigate the elemental content in different waste rock sample sizes in order to determine whether there is any substantial difference in elemental content as a function of particle size.

The samples, $D_1S_{2coarse}$ which consisted of larger particles and D_1S_{2fine} with smaller particles, were fused with $Li_2B_4O_7$ and the melts were dissolved with H_3PO_4 (**Section 5.2.5.1.1**) and the quantitative results are reported in **Table 5.11**.

5.2.5.2.2 Results and discussion

Table 5.11: The concentrations of elements

| Element | Concentration (mg/kg) | |
|---------|-----------------------|----------------|
| | $D_1S_{2coarse}$ | D_1S_{2fine} |
| Ti | 287.81 | 240.77 |
| Mn | 16.545 | 0 |
| Cu | 82.473 | 0 |
| Zr | 58.127 | 18.183 |
| Pt | 98.311 | 11.889 |
| Cr | 62.845 | 45.463 |
| U | 89.838 | 107.25 |
| Fe | 1101.3 | 1362.8 |
| Al | 7788.3 | 6026.1 |

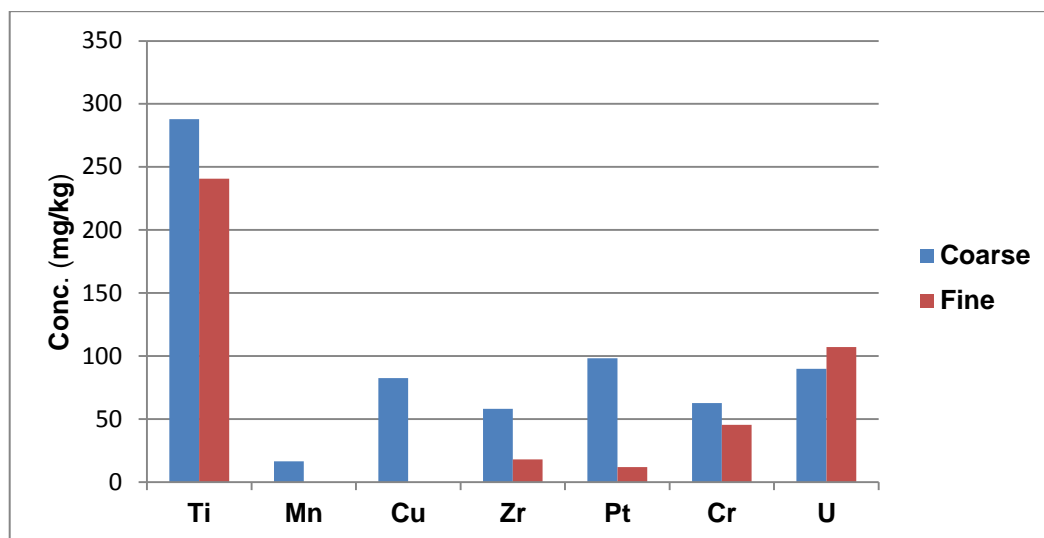


Figure 5.4: The comparison of concentrations of elements in coarse and fine particles

Figure 5.4 indicates the presence of higher concentrations of elements in bigger particles of waste rock than in smaller particles with the exception of Fe and U although the difference is not significant for most of them. The possible reason is the physical disintegration of minerals with the breaking of rocks, making it easy for the minerals to leave the bulk of the rock.

5.2.5.3 Dissolution of mine tailings by flux-fusion

The next step in this investigation involves the dissolution of the mine tailings obtained from the slime dumps close to the mines.

5.2.5.3.1 Experimental

Digestion of mine tailings samples has been investigated using flux fusion. Any moist samples were dried in an oven at 100 °C for 1 hour prior to fusion. The tailings samples were also dissolved with flux fusion using lithium tetraborate flux. In a platinum crucible, 0.5 g of the flux was mixed with accurately weighed sample (0.0999 - 0.1099 g) and manually homogenised. The mixture was heated in the furnace to a temperature of 1100 °C for 30 minutes. The crucible was then taken out of the furnace and allowed to cool on a marble bench top. The crucible was placed in a 100 mL beaker, followed by addition of dilute orthophosphoric acid (10 mL of 85%

H₃PO₄ in 60 mL ultra-pure water). The beaker was placed on a magnetic stirrer at about 80 °C for 20 minutes. The solution was allowed to cool and transferred quantitatively into a 100.0 mL volumetric flask. The flask was then filled to the mark with ultra-pure water before being allowed to stabilise for 24 hours.

The solutions were first qualitatively and then quantitatively analysed by ICP-OES. The quantitative analysis was not successful due to persistent clogging of the nebuliser, probably due to the formation of a paste by H₃PO₄ and silica. The fusion was then repeated and this time, the melt was dissolved with dilute HNO₃. This change in acid type prevented the formation of any solid material in the reaction mixture and the quantitative analysis was performed successfully (**Table 5.12**).

The dissolution of mine tailings was also repeated, but this time samples which were collected at different elevations were dissolved according to the above procedure and quantified for elemental content.

5.2.5.3.2 Results and discussion

The results in **Table 5.12** clearly indicate a smaller number of elements present in all the tailings samples, but more or less the same ones that were present in the waste rock samples. Similar to the waste rock samples, elemental content of tailings also show a domination of iron and sulphur, possibly indicating the presence of large quantities of pyrite. The results in **Table 5.12** also indicate the lower concentrations of the different elements compared to those in the waste rock samples. A possible explanation is the physical and chemical nature of the minerals/waste present on the slime dumps. All the material in the tailings is a product of previous chemical and physical treatment processes which altered the initial properties of the elements in the original ore bodies' properties. These processes most probably produced new chemical species which are more soluble in nature and are therefore more easily leached from these dump sites due to natural phenomena such as rain. These results also collaborate with those obtained for the chemical analysis of the water bodies close to the slime dumps that were investigated (**Section 5.2.7.2**). The fact that the obtained precision was unsatisfactory could be due to the high content of the flux in the solutions. The low concentrations of some of the elements in the tailings due to

leaching as well as the excessive dilution of the solutions to minimise TDS prevented accurate detection (below LOD's) for some of the elements.

Table 5.12: Elemental content of elements in the tailings samples analysed after dissolution by flux fusion

| Sample identity | Concentration (mg/kg) | | | | |
|-----------------|-----------------------|---------|-------|---------|-----------|
| | S | Ti | Cr | Mn | Fe |
| T ₁ | 240(67) | 158(2) | 31(4) | 12(1) | 841(28) |
| T ₂ | 171(23) | 177(18) | 24(2) | 11.6(9) | 951(46) |
| T ₃ | 376(104) | 102(20) | 12(3) | 66(9) | 583(86) |
| T ₄ | 180(17) | 52(13) | 0 | 14.1(4) | 430(19) |
| S ₁ | 234(29) | 99(12) | 12(1) | 78(5) | 610(53) |
| S ₂ | 490(136) | 117(11) | 19(2) | 50(8) | 1006(157) |
| S ₃ | 361(177) | 75(1) | 14(1) | 41(2) | 879(48) |
| S ₄ | 732(367) | 76(11) | 0 | 68(2) | 1731(340) |
| B ₁ | 0 | 142(4) | 16(1) | 0 | 375(9) |
| B ₂ | 0 | 144(19) | 23(3) | 0 | 571(60) |
| B ₃ | 39(10) | 87(8) | 14(1) | 7(1) | 533(39) |

() = Standard deviation

The qualitative analysis performed after using H₃PO₄ to dissolve indicated the presence of large quantities of Si, which suggests that the clogging of the nebuliser was caused by the formation of silica or silicate products in the reaction mixture. Al was omitted from the analysis, since it was regarded as being of lower value. The samples collected from the different layers or at different elevations from the ground level showed that the highest layer (second layer 3 - 6 m from ground) in general, has the lowest elemental concentration, followed by the ground level samples while the first layer (0 - 3 m) has relatively the highest elemental concentrations. **Figure 5.5** shows the concentrations of iron, chromium and titanium in the different layers of the dump. Most of the elements at all the three dumps followed the same trend. These results again point to the leaching of the elements from the higher levels in the tailing waste into the lower layer due to its exposure to rain. Possible reasons for lower leaching from the level 1 to ground may be the compacting of material (due to large volumes of material above) which is less accessible to the rain.

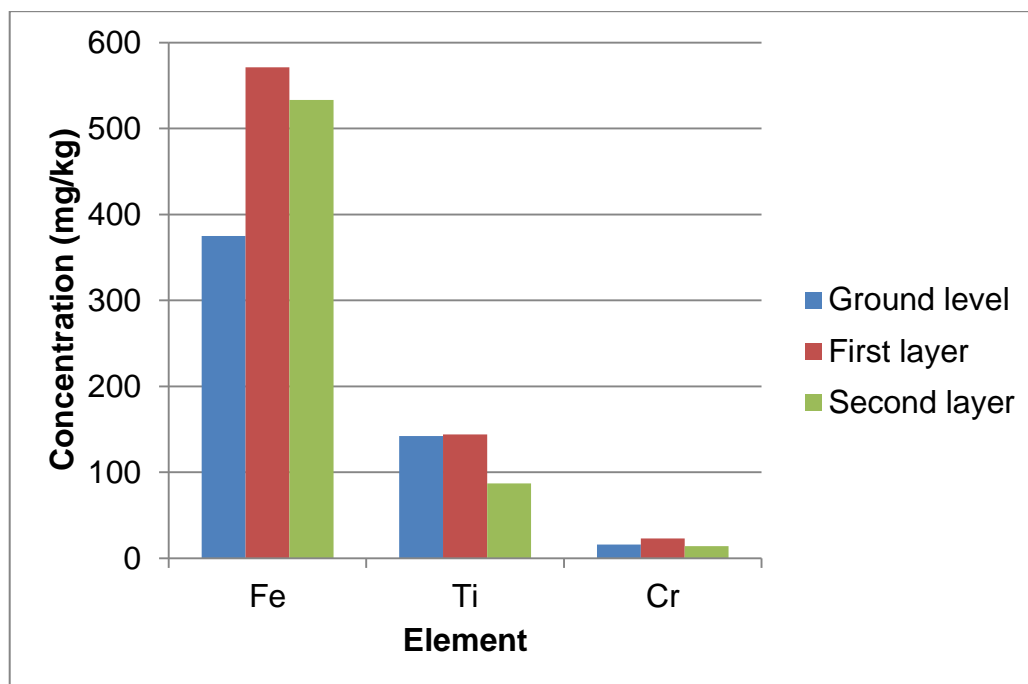


Figure 5.5: The comparison of the concentration of elements at different levels of a dump

5.2.6 ANALYSIS OF TAILINGS WITH SEM-EDS

5.2.6.1 *Experimental*

It was decided to perform a solid sample analysis on the mine tailings, which eliminates the need for any sample dissolution and the subsequent contamination and possible loss of material due to volatilisation. Three samples, namely T₂, B₂ and S₂, were analysed with SEM-EDS at the Qwa-qwa campus of the University of the Free State. Each of the samples was analysed in duplicate. A typical SEM image is presented in **Figure 5.6** while an EDS spectrum is presented in **Figure 5.7**. The results are reported in **Table 5.13**.

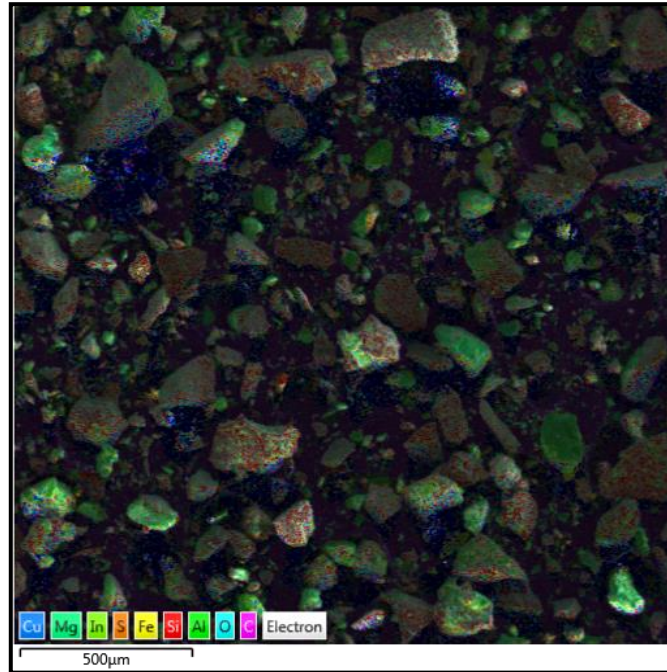


Figure 5.6: The SEM image of sample T₂

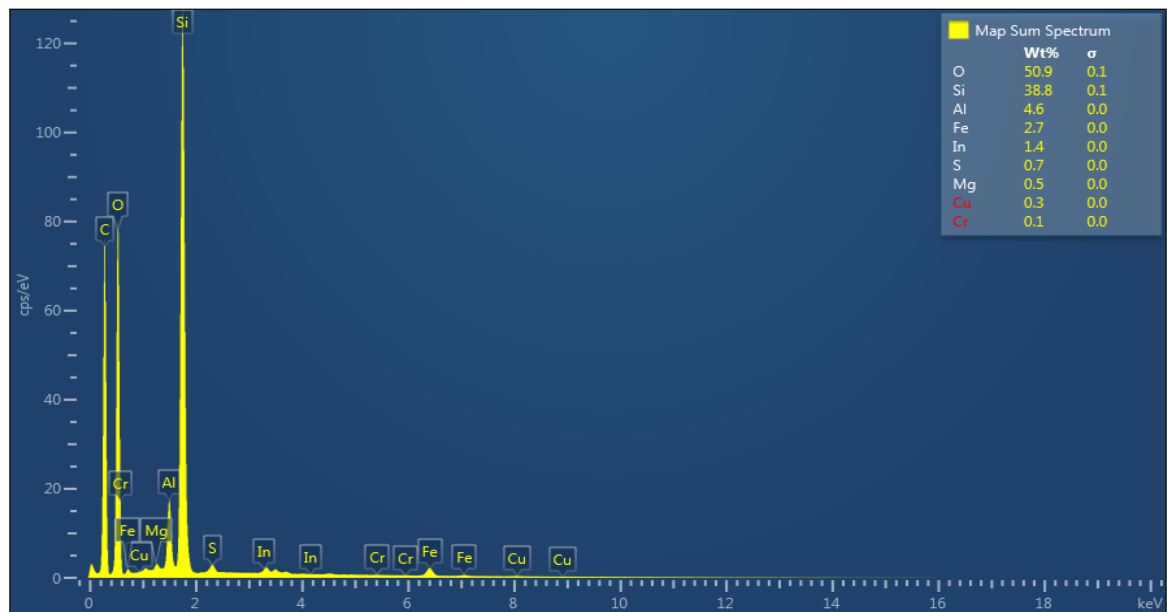


Figure 5.7: EDS spectrum of sample T₂ indicating the elemental content of the sample

5.2.6.2 Results and discussion

Table 5.13: EDS results for the tailings

| Element | Mass percent of element (%) | | |
|---------|-----------------------------|----------------|----------------|
| | T ₂ | B ₂ | S ₂ |
| O | 50.85 | 50.75 | 48.95 |
| Si | 38.55 | 39.1 | 33.95 |
| Al | 4.8 | 5.3 | 6.65 |
| Fe | 2.75 | 1.8 | 2.3 |
| Cl | - | - | 2.3 |
| Na | - | - | 1.55 |
| K | - | - | 1.5 |
| S | 0.7 | - | 1.4 |
| In | 1.4 | 1.3 | |
| Mg | 0.4 | | 0.8 |
| Cu | 0.25 | 0.5 | 0.35 |
| Ti | 0.2* | 0.2 | 0.2 |
| Mn | - | - | 0.1* |
| Mo | - | 1.2* | - |
| Cr | 0.1* | - | - |

* = Detected in only one run, - = not detected

The results in **Table 5.13** indicate high quantities of silicon, aluminium and iron in each of the three samples while trace amounts of Cr, Mn, Mo, Ti and Cu were detected, clearly indicating that the original ore bodies were dominated by the presence of silica and silicates.

5.2.7 Preparation and analysis of water samples

5.2.7.1 Experimental

The final step in this part of the study was to evaluate the water bodies near the gold mine waste sites in the Welkom area.

The water samples B_{w1} and S_w collected at the different sites were transferred into 100.0 mL volumetric flasks. HNO_3 was used to rinse the sample bottles and then added to the flasks. Samples B_{w2} and B_{w3} were shaken in the bottles filtered into 100.0 mL volumetric flasks using Munktell Ahlstrom filter papers. The filtrate solutions were allowed to stabilise for 24 hours and analysed qualitatively and quantitatively by ICP-OES. The samples B_{w4} and B_{w5} were shaken in their bottles and filtered in the same way into 100.0 mL volumetric flasks. HNO_3 was added in appropriate volumes to a total of 10 mL for matrix matching.

5.2.7.2 Results and discussion

The elemental content present in the different water bodies are reported in **Tables 5.14 and 5.15**. The results reported in the two tables clearly indicate a much wider variety of elements present in different water samples. The B_w water samples all indicate the presence of at least eleven elements with S, Fe and Mn the most abundant in almost all the samples. Also interesting is the presence of the so-called heavy metals, namely Pt, Cd, Hg as well as As. As expected, the water also contained substantial amounts of the radioactive elements Th and U.

Table 5.14: Concentrations of elements in mine water samples collected at the different mine tailing dams

| Element | Concentration (mg/L) | | | |
|---------|----------------------|-----------------|-----------------|-----------------|
| | B _{w1} | S _{w1} | B _{w2} | B _{w3} |
| P | 0.58 | 0.82 | 3.2816 | 4.8585 |
| S | 460.04 | 96.11 | 962.416 | 1204.672 |
| Ti | 0 | 0 | 1.0342 | 0.53834 |
| Cr | 0 | 0 | 0.5939 | 1.2861 |
| Mn | 20.08 | 1.28 | 74.8782 | 82.5472 |
| Fe | 0.82 | 0.1737 | 248.254 | 584.356 |
| Co | 0.56 | 0.04940 | 3.8633 | 6.3451 |
| Cu | 0.48 | 0.0982 | 10.7557 | 26.7183 |
| As | 0 | 0 | 0.1901 | 0.3066 |
| Cd | 0.0287 | 0.02704 | 0.05542 | 0.08142 |
| Pt | 0 | 0 | 3.3104 | 7.6424 |
| Hg | 0 | 0 | 0.347231 | 0.3852 |
| Pb | 0 | 0 | 0.949314 | 2.4901 |
| Th | 3.95 | 1.161 | 12.0588 | 10.9121 |
| U | 0 | 1.04192 | 0 | 5.39501 |

Table 5.15: Concentrations of elements in mine water

| Element | B_{w4} | | B_{w5} | |
|---------|-------------------------|----------------|-------------------------|----------------|
| | Conc. (mg/L) | RSD (%) | Conc. (mg/L) | RSD (%) |
| P | 1.6(1) | 8.01 | 1.67(4) | 2.56 |
| S | 855(14) | 1.69 | 734(10) | 1.38 |
| Cr | 0.045(5) | 10.7 | 0.029(3) | 10.2 |
| Mn | 16.6(4) | 2.41 | 15.6(2) | 1.05 |
| Fe | 17.2(2) | 0.97 | 100(4) | 4.11 |
| Co | 1.49(4) | 2.48 | 0.49(1) | 2.05 |
| Cu | 4.15(9) | 2.09 | 0.156(7) | 4.61 |
| As | - | | 0.156(7) | 2.28 |
| Cd | 0.048(2) | 3.75 | 0.049(3) | 5.77 |
| Pt | 0 | 0 | 1.28(6) | 4.93 |
| Th | 4.8(1) | 2.87 | 5(1) | 28.74 |

() = Standard deviation

The elemental content in samples B_{w1} and S_{w1} (collected as water only) indicates very low or concentrations of some of the elements present and no presence at all for the other analysed elements. Significantly higher concentrations of most of the elements were observed in B_{w2}, B_{w3} and B_{w4} (soil and stream-bed sediments). A possible explanation for these higher metal ion concentrations is their adsorption onto the suspended sediments in the ditches substantially increasing the metal ion concentrations.²²⁶ Previous studies indicated that the extent of adsorption of these metal ions increases with increasing pH and amount of adsorbent.²²⁷ The exceptionally high iron and sulphur concentrations in the water samples is indicative of the oxidation of pyrite in the mineral samples, which also contributes to the increase in water acidity and hence the so-called AMD.

²²⁶ C. K. Jian, V. V. Rao, B. A. Prakash, K. M. Kumar, M. Yoshida. (2010). "Metal fractionation study on bed sediments of Hussainsagar lake, Hyderabad, India", *Environmental monitoring and assessment*, 166(1-4), pp.57-67

²²⁷ C. K. Jain, D. Ram. (1997). "Adsorption of metal ions on bed sediments", *Hydrological sciences journal*, 42(5), pp.713-723

The seasonal changes tend to affect the pH of the water in these open ditches around the mine dumps. The water sample B_{w1} which was collected in winter (May) had a low pH (3.54) compared to the samples B_{w2} (6.94) and B_{w3} (6.81) that were collected in August (after some unseasonal winter rain). With lower rainfall, there is minimal dilution by either rain water or groundwater reaching the ditch (see **Chapter 2, Section 2.2**) hence an increase occurs in acidity or drop in pH. Moreover, the water level was much lower in May than in August, when the soil was wet, showing clearly that rain had fallen. Although the pH values were higher than expected, probably due to the dilution factor, corroded metal pipes in the vicinity of the water body clearly indicated high acidity levels in these water sources. A 1.0519 g soil sample from the base of dump S was mixed with 20 mL of ultra-pure water and stirred for 30 minutes. The pH measured after filtration was recorded as 2.86, clearly confirming the high acidity in the area. It is interesting to note that the high acidity is very conducive to metal ion dissolution (compared to more alkaline conditions) and its subsequent leaching from the mine tailings. This is most probably the reason for the large variety of elements present in the water samples.

From a quantitative perspective, the precision of all results for the different waste products is regarded to be satisfactory with the exception of Th. Precision decreased for the minor and trace elements.

5.3 CONCLUSION

The sample collection was carried out successfully for all the three forms of mine waste, which allowed for a comprehensive elemental study. Although the compositions of the different samples from one dump may differ, combining the samples clearly provided the average composition, thus presenting a fair reflection of the elemental content at that specific location. The leaching of different elements from the tailings due to the mineral or chemical structure alterations during the chemical extraction and recovery of gold from the ores, in the presence of water with a relatively low pH, all contribute to the transportation of the elements into the water ditches surrounding the tailings dams. The study indicates that the concentrations of

the different elements as well as the type of elements in the mine water vary with time, due to numerous factors which include the dilution extent and the pH of the water, which in turn depend on the microclimate of the places.

The study clearly indicates the presence of a number of base metals and the radioactive elements Th and U, particularly in the water bodies around the slime dumps, which can be isolated and recovered. The benefit of the re-processing of these mine dumps, or the water sources around is the fact that i) the chemical structure of the elements has been changed, making them more soluble and ii) that little or no excavation and milling is needed for its subsequent processing.

6 RECOVERY OF ELEMENTS FROM MINE WASTEWATER

6.1 INTRODUCTION

The main objectives of this study are to determine the types and quantities of the elements present in mine waste samples located around gold mines in the Welkom area, in the Free State, and to evaluate inexpensive and non-complicated methods to recover and isolate some of the more valuable elements identified in the mine waste. The results obtained from the identification and quantification of the elements in the different mine waste products (**Chapter 5**) indicated that the largest variety and amounts of the more valuable elements were present in water bodies around the slime dumps of mine tailings. A possible reason for this may be the leaching of these elements from the mine tailings as well as the high acidity of the water, which benefited elemental dissolution.

This chapter covers the final aim of this study which was to investigate the recovery/separation of elements from these water bodies according to the amounts and types of elements identified as being available in this waste product. A number of different methods were used to separate and isolate the identified elements, which included ion exchange chromatography, electrowinning, selective precipitation and selective adsorption. The analytical results obtained from the water sample B_{w3} indicated the presence of large quantities of S (1200 mg/L) and Fe (580 mg/L); moderate quantities of Mn (82 mg/L) and Cu (27 mg/L); small quantities of P (5 mg/L), Co (6.3 mg/L), Pt (8 mg/L), Th (11 mg/L), U (5 mg/L) and Pb (2 mg/L); and trace amounts of Ti (0.5 mg/L), As (0.63 mg/L) and Hg (0.4 mg/L). It was decided to investigate the possible isolation and recovery of Pt, Cu, Mn and the radioactive element Th from some of these samples due to their higher economic value and their abundance in these samples.

Quantification was carried out in respect of the various selected methods in order to monitor the separation processes and evaluate the successful isolation and recovery of the elements mentioned. The different water samples B_{w1} , B_{w2} and B_{w3} were all used according to elemental concentrations present in the samples (**Table 5.14**). For example, copper was recovered from B_{w3} , the sample which had the highest Cu concentration, while Mn was recovered from B_{w1} .

6.2 INSTRUMENTATION AND REAGENTS

6.2.1 INSTRUMENTATION

Electrowinning was performed with an electrolysis apparatus including two Pt electrodes and built-in ammeter and voltmeter. A Haldenwanger Berlin mortar and pestle set was used for crushing banana peels. A Duran desiccator was used to allow the cathode to cool in a dry environment. An oven was used for drying of banana peels and cathode while micropipettes were used to transfer samples quantitatively as well as for preparation of standard solutions. Superick borosilicate glass burettes with internal diameter 1.2 cm and 50 mL volume were used as columns in ion exchange chromatography. The ICP-OES was used for qualitative and quantitative analyses in evaluation of the success of each technique.

6.2.2 REAGENTS

The reagents which were used in this part of the study are summarised in **Table 6.1**. Standard solutions were prepared in the same way as in **Chapter 5, Section 5.2.4.1**. Dowex 66 free base resin with a styrene-divinylbenzene matrix and polyamine functional group was purchased from Sigma-Aldrich and utilised for the purpose of recovery of manganese.

Table 6.1: The information of reagents used

| Name | Formula | Purity (%) | Supplier |
|---------------------|--|------------|---------------------------------|
| Activated carbon | C | - | Merck |
| 8-Hydroxyquinoline | C ₉ H ₇ NO | 99 | |
| Glacial acetic acid | C ₂ H ₄ O ₂ | 99.7 | Associated Chemical Enterprises |
| Acetone | CH ₃ CO | 98 | Glassworld |
| Ammonium hydroxide | NH ₄ OH | 25 | Associated Chemical Enterprises |

- = information not supplied

6.3 RECOVERY OF COPPER

6.3.1 RECOVERY OF COPPER BY ELECTROWINNING

Copper has many applications in its pure metallic form and as a constituent in many metal alloys, due to its high resistance to wear and corrosion and its good electrical conductivity.²²⁸ It is extensively used in the production of electric cables and wires, ornaments, roofing and plumbing. Some alloys of copper such as brass and bronze are used to manufacture coins and gun metals.²²⁹

The electrowinning process is used widely in the mining industry to recover metals from leach solutions. It is also widely used in the metallurgical processing of wastewater streams containing high concentrations of metal ions. In electrowinning, a metal ion is deposited quantitatively by its reduction onto a working electrode. The reduction reaction for the recovery of copper is illustrated in **Equation 6.1**.²³⁰

²²⁸ J. R. Davis. (2001). Copper and copper alloys, Portland, *ASM International*, p.3

²²⁹ Periodic table. [Accessed 06-12-2018]. Available at:

<http://www.rsc.org/periodic-table/element/29/copper>

²³⁰ N. T. Beukes, J. Badenhorst. (2009). "Copper electrowinning: theoretical and practical design", *Hydrometallurgy Conference 2009*, The Southern African institute of mining and metallurgy, pp.213-240



6.3.1.1 Experimental

A 34.00 mL aliquot of the sample B_{w3} (**Table 5.14**), containing 26.7183 mg/L of Cu, was accurately transferred into a 100 mL beaker using a micropipette. A 50 mL aliquot of ultra-pure water was added, followed by 2 mL of sulphuric acid and 1 mL of nitric acid. A cylindrical gauze platinum cathode was cleaned by immersion in dilute nitric acid, then rinsed with ultra-pure water and finally with acetone, and dried in an oven at 100 °C for 5 minutes. The cathode was then placed in a desiccator for 10 minutes to cool before being weighed. The electrolysis apparatus was set up with platinum electrodes immersed in the solution and electrolysis was performed for 35 minutes with a current range 1 - 2 A while keeping the voltage below 4 V (about 2.5 V). The electrodes were lifted out of the solution while keeping a steady current, rinsed with ultra-pure water followed by acetone and dried in an oven for about 3 minutes. It was then placed in a desiccator to cool for 10 minutes and weighed to determine the amount of material deposited onto the cathode.

For identification and quantification purposes, the cathode was also immersed in dilute nitric acid for 5 minutes to dissolve all the products that had deposited onto the cathode. The solution was quantitatively transferred into a 25.00 mL volumetric flask which was filled to the mark with ultra-pure water. The solution was then quantitatively analysed by means of ICP-OES.

6.3.1.2 Results and discussion

The results obtained by weighing (gravimetry) indicate a very high percent recovery of 132% which may be due to weighing constraints with very small mass increases with the selected sample size.

The results obtained from analysis by means of ICP-OES after the dissolution of all the elements from the cathode using HNO₃ are presented in **Table 6.2**. These results indicate that not only Cu was deposited onto the cathode, but also Ti and trace amounts of other elements namely Fe, Co and Th. This clearly explains the

high recovery which was previously obtained by mass. These results are very promising, indicating very good Cu recovery from the mine waste, but also Ti recovery utilising the experimental conditions selected for this study. **Figure 6.1** depicts a platinum cathode loaded with copper. More refined experimental conditions may result in the selective recovery of the two elements.

Table 6.2: Percent recovery of elements by electrowinning analysed by means of ICP-OES

| Element | Initial Concentration (mg/L) | Concentration (mg/L) | Recovery (%) |
|---------|------------------------------|----------------------|---------------|
| Ti | 0.5383 | 0.5720 | 106.27 |
| Fe | 584.3560 | 0.1446 | 0.02 |
| Co | 6.3451 | 0.0776 | 1.22 |
| Th | 10.9121 | 0.2806 | 2.57 |
| Cu | 26.7183 | 21.6777 | 81.13 |

Bold = Most deposited elements onto cathode

Gorgievski *et al*²³¹, who used a porous copper sheet or carbon felt as the cathode, recovered more than 92% copper by electrowinning from acid mine drainage (AMD) originating from a closed copper mine, which contained a Cu concentration of 1 300 mg/L.

²³¹ M. Gorgievski, D. Bozic, V. Stankovic, G. Bogdanovic. (2009). "Copper electrowinning from acid mine drainage: a case study from the closed mine "Cerovo"", *Journal of hazardous materials*, 170(2-3), pp.716-721



Figure 6.1: Platinum cathode with deposited copper metal

6.3.2 RECOVERY OF COPPER BY PRECIPITATION

It was decided, moreover, to endeavour to isolate and recover copper using selective precipitation as method. For this purpose, oxine (8-hydroxyquinoline) was selected as precipitant or chelating agent due to its extensive application in the precipitation of metal ions present in aqueous solutions. It is utilised extensively for the concentration of Cu and its separation from other elements²³² and has been used similarly for the precipitation of aluminium. **Figure 6.2** is a presentation of the molecular structure of oxine with the chemical formula C_9H_6NOH .

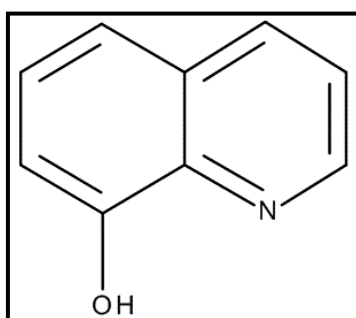
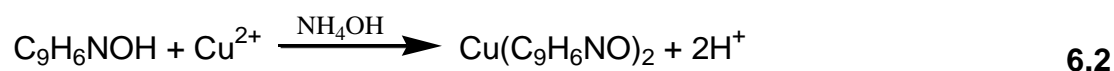


Figure 6.2: The molecular structure of 8-hydroxyquinoline

²³² F. J. Welcher, E. Boschmann. (1979). Organic reagents for copper, p.22

The removal of the hydroxide proton by bases such as ammonium hydroxide is an important step in the use of oxine as precipitant, in order to produce a negatively charged ion or chelate that reacts very easily with positively charged metal ions in solution.²³³ **Equation 6.2** illustrates the reaction between copper and oxine.



6.3.2.1 Experimental

A 3 mL aliquot of the B_{w3} mine water sample was mixed with 3 mL of 3 M oxine (acetic acid environment) in a 25 mL beaker. The mixture was heated and stirred while drops of ammonium hydroxide were slowly added until precipitate formation was visually observed. The solution was left for 10 more minutes during which time a black precipitate settled on the bottom of the beaker and the solution was filtered. The solution was left to stand overnight during which time precipitation continued. The two portions of precipitate were combined and dried. The dried precipitate was transferred into a beaker and dissolved in 10 mL of nitric acid, resulting in the formation of a yellow solution. The solution was transferred into a 100.0 mL volumetric flask and ultra-pure water was added up to the mark. The solution was quantitatively analysed by means of ICP-OES. The results are reported in **Table 6.3**.

6.3.2.2 Results and discussion

The quantification of the elements present in the dissolved oxine precipitate clearly indicated the presence of a variety of elements, including Cu. Oxine was successful in recovering copper together with iron and cobalt, and a bit of sulphur.

²³³ D. Sobhana, P. M. Madhusoodanan, C. S. P. Iyer. (2003). Thermal studies of some inorganic organic compounds. University of Kerala, p.2

Table 6.3: The percent recoveries of elements from the B_{w3} sample by precipitation with oxine

| Element | Concentration (mg/L) | Concentration in water (mg/L) | Recovery (%) |
|-----------|----------------------|-------------------------------|--------------|
| S | 66.37933 | 1204.672 | 5.51 |
| Fe | 521.6433 | 584.356 | 89.27 |
| Co | 3.468133 | 6.34514 | 54.66 |
| Cu | 15.20043 | 26.7183 | 56.89 |

Bold = element of interest

Although the target element in this step of the study was copper and while co-precipitation of Fe, Co and S also took place, the reaction with oxine showed some selectivity since out of the fifteen present, only these four elements in B_{w3} (with the highest concentrations - **Table 5.14**) were isolated. The isolated precipitate was mainly black with greenish specks in between. Previous studies indicate that elemental isolation with oxine in weakly acid conditions can be very successful.²³⁴ Although pH was neither closely monitored nor controlled in this study, the initial pH of the sample was measured to be below 1 while the addition of NH₄OH (removal of hydroxide proton) yielded the precipitate. The formation of the mixed precipitate containing Fe, Co and Cu may be due to the fact that they precipitate in the pH range of 2.5 - 3.6²³³ and that a better control of pH may result in better selectivity.

6.4 RECOVERY OF MANGANESE BY ION EXCHANGE CHROMATOGRAPHY

Manganese is a transition element which occurs naturally in the earth's crust, constituting about 0.085%.²³⁵ Manganese is too brittle to be used in its metallic form and is therefore used mainly in the production of alloys which are used extensively, including different types of steel. MnO₂ and LiMn₂O₄ are also extremely important in

²³⁴ J. E. Grindler. (1962). The radiochemistry of uranium, National academy of sciences, p.53

²³⁵ R. D. W. Kemmitt, R. D. Peacock. (1973). The chemistry of manganese, technetium and rhenium, Pergamon press, p.771

energy storage and widely used in the production of alkaline batteries^{236,237} and lately in batteries for electric cars such as the Tesla.²³⁸ Ion exchange chromatography has found many applications which generally entail the separation of metal ions in a multi-ionic solution. It has been employed traditionally for water purification and removal of metal ions contaminating waste waters. For example, it is used for removal of copper and zinc in the recovery of cobalt, prior to its electrowinning recovery.²³⁹

The recovery of manganese from the B_{w1} mine water sample (**Table 5.14**) was carried out using ion exchange chromatography. The B_{w1} mine water sample did not have the highest, but was selected for this part of the study due to its sufficient concentration of only Mn (20 mg/L), in order to save other samples for recovery of other elements. The efficiency of this method of the selective recovery Mn was discovered by Nete *et al*²⁴⁰ using the Dowex 66 free base resin in a phosphate matrix. They reported a total recovery efficiency of 97.5% Mn₃O₄ which was obtained by elution with 0.5 M H₃PO₄

6.4.1 EXPERIMENTAL

A portion of the Dowex 66 free base anion exchange resin was transferred into a 100 mL beaker. Ultra-pure water was added to cover the resin and the slurry was transferred into a 50 mL burette. In this process, the tap was opened to release some of the water. This was done repeatedly while tapping the column (burette) to pack the resin until the resin height was 15 cm. The resin was activated by using

²³⁶ B. Grimsmo. (2014). Life cycle assessment of Li-ion batteries for electric vehicles, Master thesis, Norwegian university of science and technology, p.20

²³⁷ D. Stephens, P. Shawcross, G. Stout, E. Sullivan, J. Saunders, S. Risser, J. Sayre. (2017, October). Lithium-ion battery safety issues for electric and plug-in hybrid vehicles. Washington, DC: National Highway Traffic Safety Administration, p.2-5

²³⁸ L. Jayanti, How battery chemistry is driving tesla car revolution?. [Accessed 09-01-2019]. Available at: https://www.slideshare.net/sreekanth_j/chemistry-of-tesla-batteries

²³⁹ K. C. Sole, M. B. Mooiman, E. Hardwick. (2016). "Present and future applications of ion exchange in hydrometallurgy: an overview", Society of Chemical industry, IEx 2016 - Hydrometallurgy session

²⁴⁰ M. Nete, W. Purcell, J. T. Nel. (2017). "Non-Fluoride dissolution of tantalum and niobium oxides and their separation using ion exchange", *Hydrometallurgy*, 173, pp.192-198

previously prepared 0.5 M phosphoric acid and the flow-rate was adjusted to about 0.67 mL/min. A 5.00 mL aliquot of mine water B_{w1} was transferred into the column using a micropipette. Elution was carried out using the 0.5 M phosphoric acid while collecting 10 mL fractions with 100.0 mL volumetric flasks. Ultra-pure water was used to dilute the fractions to the mark of each flask. The solutions were qualitatively and then quantitatively analysed for elemental content.

6.4.2 RESULTS AND DISCUSSION

The qualitative analysis of the fractions collected from 15 to 45 minutes indicated only the presence of Mn in the solution (**Figure 6.2**). The quantitative analysis clearly indicated the selective isolation of manganese from this wastewater sample and a total of 77(7)% of the Mn was recovered (average of four replicates) with a precision (RSD) of 8.59%.

The Dowex 66 resin is a weak base anion exchange resin that works optimally in acidic to neutral pH. The chromatogram obtained for the first run (74% recovery) is presented in **Figure 6.3**. From these results, it is clear that ion exchange chromatography is very effective in terms of selectivity and the good recovery of Mn in these types of waste samples. Although the study did not recover 100% Mn, the highest of the four replicates gave a recovery of 85%. Another advantage of the method is time-effectiveness as Mn was the first element to be eluted. Thus, no time-wasting occurred and the dead time of the column was very short. However, the method saves reagents, as the minimal eluent volume is required for this extraction and isolation.

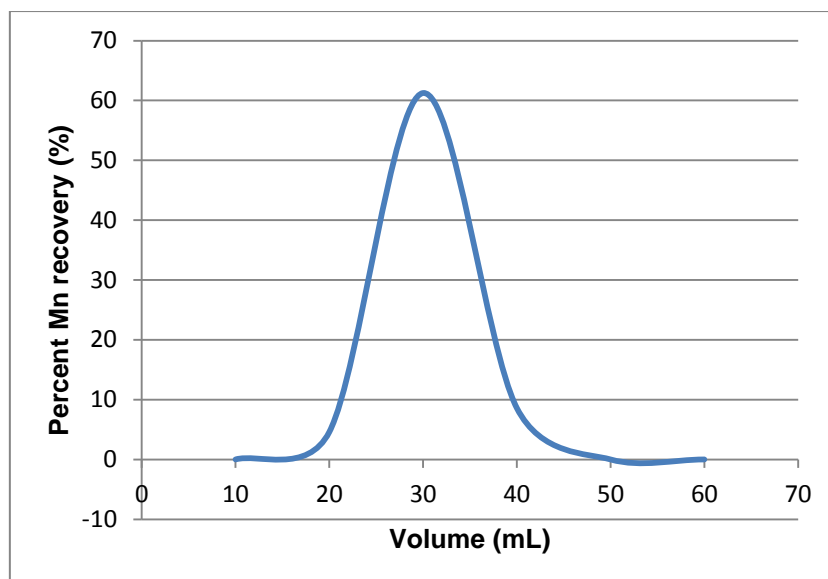


Figure 6.3: Chromatogram for the Ion exchange chromatography recovery of Mn

6.5 RECOVERY OF PLATINUM BY ADSORPTION

Platinum is a precious metal and the most commonly used of the six platinum group metals. It is highly unreactive in nature, therefore very resistant to corrosion, tarnish and wear.²⁴¹ Platinum is used to make cancer-treating drugs such as cisplatin and carboplatin²⁴², in the making of jewellery, in catalytic converters of automobiles as well as in the electrical contacts and electrodes.²⁴³

Activated carbon is a material made up of carbon atoms, and is processed to have low-volume pores in order to increase the surface area for adsorption.²⁴⁴ It is manufactured from carbonaceous materials such as charcoal, by the removal of all non-carbon impurities and oxidising the surface either thermally or chemically (using

²⁴¹ Why is platinum so expensive? International precious metals. [Accessed 10-01-2019]. Available at: <https://www.preciousmetals.com/blog/2015/01/platinum-expensive/>

²⁴² T. C. Johnstone, G. Y. Park, S. J. Lippard. (2014). "Understanding and improving platinum anticancer drugs – phenanthriplatin", *Anticancer research*, 34(1), pp.471-476

²⁴³ Platinum and its use. [Accessed 10-01-2019]. Available at: <https://www.totalmateria.com/page.aspx?ID=CheckArticle&site=ktn&NM=237>

²⁴⁴ H. Marsh, F. Rodriguez-Reinoso. (2006). Activated carbon, 1st ed., London, UK, *Elsevier Ltd*, p.2

phosphoric acid).²⁴⁵ Activated carbon is a well-known and preferred adsorbent for its large surface area, high adsorption capacity, low cost and high purity, porous structure and negligible environmental toxicity. Snyders *et al*²⁴⁶ succeeded in the adsorption of 100% platinum from an alkaline cyanide leach solution containing 0.38 mg/L Pt by a 72 hour long traditional rolling method.

6.5.1 EXPERIMENTAL

An accurately weighed 0.4010 g portion of activated carbon was stirred with 12.5 mL of the B_{w3} mine water sample for 3 hours at a temperature of 80 °C. The mixture was allowed to cool and filtered into a 25 mL volumetric flask and the residue was washed with ultrapure water. A 2.5 mL aliquot of HCl was added and the flask was filled to the mark with ultra-pure water. The solution was allowed to stabilise overnight and then analysed by ICP-OES.

6.5.2 RESULTS AND DISCUSSION

The results in **Table 6.4** clearly indicate that numerous elements present in B_{w3} were adsorbed by the activated carbon. The adsorption of platinum on the activated carbon was not very efficient as only 17% Pt was adsorbed, which was comparatively low compared to 99% as reported by Aktas and Morcali.²⁴⁷ The results, moreover, indicated that all the Hg in the initial sample was adsorbed, as well as fairly high recovery of Cd (82%) and As (60%) which are all deemed toxic. Th and U were also adsorbed although the extent was quite low (21 and 38% respectively).

²⁴⁵ F. Cecen, O. Aktas. (2012). Activated carbon for water and wastewater treatment: integration of adsorption and biological treatment, 2nd ed., , Weinheim, Germany, *Wiley-VCH Verlag GmbH & Co. KGaA*, p.1

²⁴⁶ C. A. Snyders, C. N. Mpinga, S. M. Bradshaw, G. Akdogan, J. J. Eksteen. (2013). "The application of activated carbon for the adsorption and elution of platinum group metals from dilute cyanide leach solutions", *Journal of the Southern African institute of mining and metallurgy*, 113(5), pp.381-388

²⁴⁷ S. Aktas, M. H. Morcali. (2011). "Platinum recovery from dilute platinum solutions using activated carbon", *Transactions of nonferrous metals society of China*, 21, pp.2554-2558

Table 6.4: The concentrations and recoveries from the B_{w3} sample of elements in the post-adsorption filtrate

| Element | Conc. (mg/L) | Initial Conc. in B _{w3} (mg/L) | Recovery in filtrate (%) | Percent adsorbed (%) |
|---------|--------------|---|--------------------------|----------------------|
| Ti | 0.536112 | 0.538337 | 99.59 | 0.41 |
| Cr | 1.093318 | 1.28611 | 85.01 | 14.99 |
| Co | 5.3851 | 6.34514 | 84.87 | 15.13 |
| Cu | 25.5928 | 26.7183 | 95.79 | 4.21 |
| As | 0.122544 | 0.306608 | 39.97 | 60.03 |
| Cd | 0.01462 | 0.081423 | 17.96 | 82.04 |
| Pt | 6.33322 | 7.64242 | 82.87 | 17.13 |
| Hg | 0.00 | 0.385156 | 0.00 | 100 |
| Th | 8.61336 | 10.9121 | 78.93 | 21.07 |
| U | 3.35666 | 5.39501 | 62.28 | 37.78 |

Conc. = concentration

Activated carbon has been used successfully to remove heavy metals including Cd, Cu, Hg, Ni and Pb from industrial wastewaters.²⁴⁸ Based on the results in this part of the study, it can be used to decrease the degree of contamination in mine water, while also recovering the elements. Activated carbon therefore proved to be a good adsorbent for the treatment of wastewater containing potentially toxic elements.

6.6 RECOVERY OF THORIUM BY ADSORPTION AND DESORPTION

Thorium is a slightly radioactive metal which is mainly commercially extracted from the mineral monazite while other minerals, such as thorite and thorionate, exist.²⁴⁹ Thorium may be used in the production of nuclear power as it is more

²⁴⁸ K. Kadirvelu, K. Thamaraiselvi, C. Namasivayam. (2001). "Removal of heavy metals from industrial wastewaters by adsorption onto activated carbon prepared from an agricultural solid waste", *Bioresource technology*, 76(1), pp.63-65

²⁴⁹ Thorium. [Accessed 10-01-2019]. Available at: <https://www.britannica.com/science/thorium>

environmentally friendly than uranium.²⁵⁰ It may also be used in high quality optical lenses due to its high refractive index. Due to its strength and creep resistance to high temperatures, Th constitutes an alloy with magnesium, which is used in aircraft and rocket engines.²⁵¹

Crushed banana peel, a common biological waste, has been used as an adsorbent for some potentially toxic heavy metal ions, which include Cu, Pb, Cd and Cr, from aqueous solutions.²⁵² This adsorbent has also been used successfully for the removal of the radioactive elements, U and Th, from mine water, resulting in 99.9% Th and 70% U removal at pH 3.0.²⁵³ In addition to the effectiveness, banana peel sorbent has a low cost as it is a waste material in the food industry.²⁵⁴

6.6.1 ADSORPTION OF THORIUM ONTO BANANA PEELS

6.6.1.1 Experimental

Banana peels were rinsed with ultra-pure water, cut into pieces of about 1 cm in length and width and oven-dried at 50 °C for 24 hours. The dry pieces were then crushed using mortar and pestle. Accurately weighed 4 g portions of the crushed banana peels were added to mine water B_{w2} (12.5 mL) and stirred for 3 hours at room temperature. The mixtures were filtered into 25.00 mL volumetric flasks. Three 1.25 mL aliquots of nitric acid were added to the filtrates in the flasks. Ultra-pure water was added up to the mark of each flask. The solutions were analysed by means of ICP-OES.

²⁵⁰ Thorium nuclear fuel tests almost complete and successful. [Accessed 10-01-2019]. Available at: <https://www.steenkampskraal.com/thorium-nuclear-fuel-tests-almost-complete-successful/>

²⁵¹ J. Arnold, T. L. Gianetti, Y. Kashtan. (2014). "Thorium lends a fiery hand", *Nature chemistry*, 6, p.554

²⁵² G. Crini, E. Lichtfouse. (2018). Green adsorbents for pollutant removal: fundamentals and design, *Springer international publishing*, p.205

²⁵³ O. A. Oyewo, M. S. Onyango, C. Wolkersdorfer. (2016). "Application of banana peels nanosorbent for the removal of radioactive minerals from real mine water", *Journal of Environmental Radioactivity*, 164, pp.369-376

²⁵⁴ P. Kumari. (2017). "A low cost material, banana peel for the removal of lead (II) from aqueous solutions", *International research journal of engineering and technology*, 4(6), pp.1404-1406

6.6.1.2 Results and discussion

The adsorption using banana peels was attempted initially by using a column. The outcome was negative as the banana peels became sticky as they got wet, absorbed a lot of water and grew in size. This caused compaction in the column and the feed solution could not be eluted. It was then decided to perform the experiment by stirring the mine water in the presence of banana peels in a beaker. The peels still absorbed a lot of the solution, making it difficult to stir. More water was added to the mixture when almost all of it was absorbed. The percent recovery of each element in the filtrate is reported in **Table 6.5**.

Table 6.5: The percent recovery from the B_{w2} mine water sample in the post-adsorption filtrate per element

| Element | Recovery in filtrate (%) | Percent adsorbed (%) | SD(%) | RSD (%) |
|---------|--------------------------|----------------------|-------|---------|
| Ti | 18.92 | 81.08 | 8.57 | 10.57 |
| Cr | 5.20 | 94.80 | 8.59 | 9.06 |
| Mn | 35.41 | 64.57 | 9.17 | 14.19 |
| Co | 26.98 | 73.02 | 8.67 | 11.87 |
| As | - | 100 | - | - |
| Cd | 21.05 | 78.95 | 36.46 | 46.18 |
| Pt | 11.36 | 88.64 | 6.85 | 7.73 |
| Hg | 21.66 | 78.34 | 37.52 | 47.90 |
| Th | 38.63 | 61.37 | 13.35 | 21.76 |

- = not detected

SD - Standard deviation

RSD - Relative standard deviation

The results in **Table 6.5** indicate little selectivity with nine of the fourteen elements being partially adsorbed by the banana peels. While the Fe and S concentrations were too high to be measured, there were challenges in quantifying the other elements. The overall order of adsorption was As > Cr > Pt > Ti > Cd > Hg > Co > Mn > Th. In most cases in this study, the precision was unsatisfactory with RSDs as high as 22% for Th and 48% for Hg. As anticipated following previous studies, the

process successfully removed 61.4% of the Th, but it was more successful in removing the As present in the mine waste. On the positive side, this method proved that the use of banana peels as adsorbent can be effective in the partial clean-up of waste water samples.

Research results indicate that banana peels were successfully used as adsorbent for the removal of Cd²⁵⁵, Cu, Co, Ni, Zn, and Pb from water samples.²⁵⁶ Abbas²⁵⁷ removed 95.34% synthetic Th(NO₃)₄•5H₂O sample solution by a column adsorption method using banana peels, with an initial concentration of 1 mg/L.

The lower than expected Th removal of 61.4% in the current study could be due to the much higher Th concentration in this study (12.06 mg/L), as well as to interference by the other elements in the sample, which was not the case in Abbas' study

6.6.2 DESORPTION OF THORIUM FROM BANANA PEEL SORBENT

Desorption, in this case, entails the release of previously adsorbed metal ions from the surface of the banana peel sorbent into solution. It is a fundamental method in the recovery of elements in cases whereby sorption has been applied previously. The recovery of Th from the peels was performed using H₂SO₄.

6.6.2.1 Experimental

The loaded banana peels obtained from the previous study were air-dried for three days. They were then transferred into a beaker before 3.68 M sulphuric acid was added and the mixture was stirred for 1.5 hours. More water was added to allow for

²⁵⁵ J. Anwar, U. Shafique, W. Uz-Zaman, M. Salman, A. Dar, S. Anwar. (2010). "Removal of Pb(II) and Cd(II) from water by adsorption on peels of banana", *Bioresource technology*, 101(6), pp.1752-1755

²⁵⁶ G. Annadurai, R. S. Juang, D. J. Lee. (2003). "Adsorption of heavy metals from water using banana and orange peels", *Water science and technology*, 47(1), pp.185-190

²⁵⁷ F. S. Abbas. (2013). "Thorium removal from waste water using banana peel and employment of waste residue", *Advances in natural and applied sciences*, 7(3), pp.336-344

the stirring of the mixture as the peels continuously absorbed the liquid. The mixtures were filtered into 25.00 mL volumetric flasks and were each washed with two 5 mL aliquots of ultra-pure water. Ultra-pure water was added to the filtrates in the flasks, allowed to stand overnight and analysed by means of ICP-OES.

6.6.2.2 Results and discussion

The results obtained from elemental recovery from the banana peels are reported in **Table 6.6**. All the elements that were partially adsorbed by the initial process were now desorbed but not in the same quantities as expected. The results indicated that only 28% of the adsorbed Th was recovered from the banana peels, while elements such as Cr and As were completely retained on the peels. The precision had generally improved in this part of the recovery, especially for Th. A 96% desorption rate of Th from deoiled karanja seed cake was attained by Varala *et al*²⁵⁸ by using 1 M HCl.

Table 6.6: The recovery of elements in filtrate from banana peel sorbent after desorption

| Element | Recovery (%) | SD (%) | RSD (%) |
|---------|--------------|--------|---------|
| Ti | 24.04 | 5.06 | 21.03 |
| Cr | - | - | - |
| Mn | 39.15 | 5.21 | 13.30 |
| Co | 26.17 | 6.25 | 23.87 |
| As | - | - | - |
| Cd | 110.33 | 45.33 | 41.09 |
| Pt | 21.77 | 5.38 | 24.73 |
| Hg | 60.74 | 14.70 | 24.19 |
| Th | 28.08 | 4.09 | 14.58 |

- = not detected

SD - Standard deviation

RSD - Relative standard deviation

²⁵⁸ S. Varala, S. K. Bhargava, R. Parthasarathy, B. Satyavathi. (2017). "Desorption studies for the recovery of thorium from loaded biosorbent (DKSC): parameter optimization and equilibrium modelling", *International journal of advances in science engineering and technology*, 5(3), pp.55-57

6.7 CONCLUSION

The ultimate aim of this part of the study was to isolate and recover some of the identified elements in the mine wastewater samples. Cu and unintentionally 100% Ti as contaminant was successfully recovered by electrowinning. The selective precipitation of copper using oxine was less successful with the co-precipitation of iron, cobalt and sulphur. Manganese was successfully isolated and recovered using ion exchange chromatography. Arsenic was successfully adsorbed with activated carbon while banana peels succeeded in the removal of a large number of elements in the wastewater with varying degrees of success, but little selectivity was observed. Activated carbon also proved to be an effective adsorbent for Hg, Cd and As compared to its Pt removal.

All the methods were successful in recovery of the selected target elements although selectivity was lacking in all the studies with the exception of the Mn recovery. The extent of elemental recovery (accuracy and precision) was also adversely affected, moreover, by the low concentrations of the elements in the mine water.

The methods which were investigated in this part of the study were regarded as fit for recovery of the more valuable elements in the waste water samples while capable of decreasing the degree of contamination of mine water.

7 EVALUATION OF THE STUDY AND FUTURE RESEARCH

7.1 INTRODUCTION

The aim of this chapter is to evaluate the degree of success of this study as a whole, by comparing the initial aims and objectives of the study, as outlined in **Chapter 1, Section 1.4**, against the results obtained in the study. The chapter further deals with possible future research emerging from this study.

7.2 EVALUATION OF THE STUDY

The aim of the study was to evaluate the elemental content in the different types of waste at gold mine waste dumps at the Welkom/Virginia area as well as the possible recovery of the more valuable and useful elements identified in the mine waste. The objectives were outlined as follows:

- To investigate the elemental composition of the waste rock dumps and tailings in order to identify any valuable elements that may be present
- To identify suitable dissolution methods for the different solid waste products.
- To determine the concentrations of the identified elements in the waste
- To analyse the drainage water or dry drainage bed beside the dumps to investigate possible leaching of metals from the dumps into the streams
- Investigation of different techniques for the beneficiation of some of the valuable metals present in the waste samples.

The study is regarded as successful if the results in **Chapters 5 and 6** are compared with the above objectives. Three different kinds of mine waste samples, namely waste rock, tailings and mine water, were collected at different gold mines in the Free State. The waste rock samples were dissolved completely with the flux-fusion technique. Numerous fluxes and acids were employed to dissolve the waste rock samples, some proving more successful than others. Fusion with the potassium fluoride flux and subsequent dissolution with sulphuric acid (H_2SO_4) yielded a clear solution but was abandoned for safety purposes. Similarly, sodium peroxide fusion was successful in the complete dissolution of the samples, but was abandoned to avoid any possible contamination as the resulting solution was black, and the crucible could have contributed. Finally, lithium tetraborate flux was used for the complete sample dissolution at 1 100 °C, the melt was dissolved completely with dilute phosphoric acid (H_3PO_4) and analysed by means of ICP-OES. Results obtained from this step of the study indicate the presence of large quantities of Al, Fe and S and smaller amounts of Mn, Ti, Cr and Th.

Fusion of tailings collected at the mine sites was also performed with lithium tetraborate and the melt was dissolved with H_3PO_4 . Elemental analysis using this combination was unsuccessful due to the clogging of the nebuliser. Nitric acid was then used to replace the H_3PO_4 and the samples were analysed by means of ICP-OES. A similar set of elements was present in these tailings samples with significant amounts of Fe and smaller amounts of S, Cr, Ti and Mn. An elemental study at different heights of the mine slime dump indicated the systematic leaching of soluble elements from the higher to lower levels. No evidence of gold was found, most probably due to its very low concentration levels in the waste material.

The final waste samples analysed were the water samples collected around the mine slime dumps. The ICP elemental analysis indicated the presence of a larger number of elements, probably leached from the slime dumps, which included Mn, Cu, Th, U, Cr, and a number of heavy metals such as As, Pb and Hg. It was found that the elemental content of the initially sedimented water samples differs substantially from that of the initially unsedimented water samples.

A number of more valuable elements such as Mn, Cu, Th and Ti were identified for possible recovery from these water waste samples. Ion exchange chromatography (IEC) was used to isolate and recover manganese selectively from the mine water sample using the Dowex 66 free base resin. The column was packed and activated with 0.5 M H_3PO_4 . The elution was carried out, using 60 mL of 0.5 M H_3PO_4 . The method was successful, eluting Mn as the first element and a maximum recovery of 86% was obtained.

Copper was recovered from mine water using electro-winning. This method was successful in the recovery of 81% Cu, while a large amount of Ti. Cu was also isolated using 0.3 M oxine in acetic acid as precipitant, which likewise proved to be successful although, in this case, the method co-precipitated iron, cobalt and sulphur.

Activated carbon adsorption was used to recover platinum from mine water by stirring at 80 °C but resulted in low Pt recovery. However, the method succeeded in the removal of other elements such as Hg, Cd and As. Finally, the isolation and recovery of thorium was investigated, using banana peel as possible sorbent. Although the recovery of Th was relatively low (60%), the method proved to be effective in the removal of other elements such as As, which was completely recovered. Desorption with H_2SO_4 yielded only 28.08% Th recovery from the loaded banana peels.

7.3 FUTURE RESEARCH

The possible research studies that may emanate from and complement this study are outlined below:

- Quantification of waste rock by dry analysis techniques to avoid challenges brought about by matrix effects

- Quantitative recovery of both Cu and Ti by means of electro-winning, by employment of different experimental conditions
- Increasing the recovery of Mn by varying the column properties as well as concentration of the feed
- Separation of Co, Cu and Fe in the oxinate matrix under different experimental conditions, especially the working pH
- Recovery of Th by solvent extraction.

SUMMARY

Mining activities normally produce large quantities of different waste products after the separation and isolation of the economically valuable elements present in the mineral ores. The mine waste dumps do not only tarnish the natural environment, but also have the capacity to liberate potentially harmful elements which contaminate local natural resources such as water and air. However, the same waste may also be a source of economically valuable elements which have been mined simultaneously with other valuable elements (then target elements), but were not of any economic importance during the previous mining activities.

The aim of this study was to determine the elemental composition of gold mine waste material in the Free State. The possible separation and isolation of some of the more valuable elements in waste material also formed a part of the study. Samples were collected from various dump sites near Welkom in the Free State. Flux-fusion decomposition was extensively employed in the dissolution of the solid samples and the elemental contents of these samples were determined, using the inductively coupled plasma optical emission spectrometer (ICP-OES) for elemental content. The water samples were also analysed with the same instrument. The ICP-OES was used throughout the study in order to monitor and evaluate the success of numerous separation techniques which were carried out to recover some of the valuable elements.

Waste dumps in the Welkom/Virginia are in the Northern Free State were selected for this study. Waste rock sampling was carried out at six dump sites, where five samples were randomly collected at various points in order to include waste with different particle-sizes and surfaces colours. The sub-samples were milled and equal masses of those taken from one site were combined and homogenised manually. Tailings were collected at three dumps from different layers. Mine water samples were also collected at two sites in ditches surrounding the tailings.

Summary

Decomposition by flux-fusion was carried out with different fluxes, some of which did not dissolve the waste rock completely. Lithium tetraborate ($\text{Li}_2\text{B}_4\text{O}_7$) was used for the waste rock samples and the resulting melts were dissolved with H_3PO_4 . The tailings were also decomposed with $\text{Li}_2\text{B}_4\text{O}_7$ and the melts were dissolved with HNO_3 . Water samples were acidified immediately after collection and those that were collected with sediments were filtered. All the samples were analysed by means of ICP-OES.

The waste rock generally contained, Cr, Mn, Zr, Pt, Th, with significantly high concentrations of Al, S, Ti and Fe. The tailings generally comprised Ti, Cr, Mn and high concentrations of Fe and S. The EDS spectrum indicated the presence of a very high concentration of Al. Many more elements with various degrees of economic importance were found in the water samples collected in the vicinity of the tailings dams. Elements identified in these water samples with stream bed sediments included P, S, Ti, Cr, Mn, Fe, Co, Cu, As, Cd, Pt, Hg, Pb, Th and U.

Electro-winning was carried out to recover copper selectively from mine wastewater, using electrolysis apparatus with platinum gauze electrodes, resulting in a copper recovery of 81.13% and a Ti recovery of 106.27%. In another part of the study, oxine, in the presence of NH_4OH , was used in the selective precipitation of copper in an acetic acid matrix. The analysis of the dissolved precipitate in HNO_3 revealed the presence of Fe, Co and S in the precipitate. The recoveries of 56.89% Cu, 5.51% S, 89.27% Fe and 54.66% Co were obtained.

Manganese was recovered selectively by ion exchange chromatography using the Dowex 66 free base anion exchange resin and 0.5 M orthophosphoric acid for elution. This resulted in the Mn recovery of 77(7)%. Adsorption of Pt onto activated carbon was attempted, at an elevated temperature. This procedure was not regarded as effective as since only 17% Pt was adsorbed, while many other elements were also adsorbed, leading to lack of selectivity. The use of banana peel as sorbent for Th was also attempted. The sorbent was prepared by rinsing, drying and crushing banana peels, for use as possible sorbent. Analysis of the filtrate revealed adsorption of various elements,

Summary

the adsorption percentage of Th being 61.37%. These results indicated lack of selectivity within the method. Desorption of the elements from the loaded banana peel sorbent with H_2SO_4 resulted in 28.08% Th recovery, while larger recoveries were obtained for Cd, Hg and Mn.

From this study, it is clear that mine waste dump sites may be a valuable source of economically valuable elements. Moreover, very modest hydrometallurgical methods may be used in the isolation and recovery of these elements, thus making mine waste sites valuable alternative elemental sources with economic value.