BSc. Thesis applied earth sciences

TA3006-10  DE-XRT assessment on porphyry copper ore from Chile

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Abstract

In order to find a solution to the problem of decreasing grades, increasing ore-to-waste-ratios and increasing mining and mineral processing costs, de mining industry shows great interest in new technical solutions to add value to their products. One of the most promising technical innovations is the use of sensor based sorting operations. With sensor based sorting it is possible to separate single particles based on their physical properties.

There are several sensor based sorting operations, all based on different physical principles. Examples are NIR-spectroscopy, XRF-fluorescence spectroscopy and XRT. The focus in this report is on DE-XRT (dual-energy x-ray transmission). With this technique a low energy as well as a high energy image is made from an object trough which x-rays have been transmitted. The amount of absorption is measured, this depends on atom number, density and particle thickness. When using the absorption results of the high and low energy image, the thickness can be ignored, this can be proved mathematically with the law of Lambert-Beer.

The samples which are investigated are porphyry copper ores from The Los Broncos mine in Chile. These ores belong to the category of the hydrothermal ore deposits. These deposits owe their genesis to hot aqueous solutions. Porphyry copper deposits are a subgroup of the hydrothermal deposits, they are related to sub volcanic intrusions which have risen to a high level in the crust. Fluids exsolved from cooling magma contribute to hydrothermal alternation of minerals in the apical region, and to the formation of different mineralogical zones.

There measurements have been performed with the DE-XRT scanner in the Stevin lab at the TU Delft. Each sample has been scanned twice, the second time in another direction in order to deal with anisotropic effects. The output consists of a low and a high energy image which contain 16-bit (max.4096 counts) data. These counts are directly related to absorption. A TU Delft in house sort application is used to process the data. When a threshold of 500 counts is applied, every value below 500 counts is set to zero, this leads to significant decrease in variability in the output data, consisting of the effective atom number, the standard deviation of this number and the differences between the average atom number values between measurements from different directions.

When the Zeff is plotted in a scatter with the copper grade, an R-squared value of 0.05 is obtained, which indicates that there is no significant correlation between them. Addition of the iron grade leads to an R-squared vale of 0.78, which is significantly higher. An explanation for this could be the fact that iron and copper occur together in the most abundant ore mineral chalcopyrite. When a grouping of ore and waste samples is applied to the scatter of the metal grades versus Zeff, firstly based on NIR ore probability and than on copper grade, it can be noticed that based on DE-XRT an extra 12% of the samples can be classified as waste compared to NIR when a threshold of Zeff<12.5 is applied to the sorting process. However, further investigation will be needed because of the limited data set of 58 samples and the irregularity in shape of the samples, which made it difficult to do well described directional measurements.
Preface

This report is about a DE-XRT assessment on Porphyry copper ore from Chile. Earlier work regarding sensor based sorting is done by Marinus Dalm in his MSc. Thesis on *Applicability of near-infrared spectroscopy for sensor based sorting on mill pebbles from the Los Broncos copper mine, Chile*. One of the goals of this report is to investigate if DE-XRT can be a useful tool to separate ore from waste rock when used in combination with NIR-spectroscopy, which could possibly give some new interesting views on the topic.

Performing the lab tests as well as the completion of this report would not be possible without the help of some dedicated members from the scientific staff of the department of geotechnology at the TU Delft. First of all, I would like to thank Dr. Mike Buxton and PhD. Candidate Marinus Dalm for their tips and support during my research. I am also grateful to Joost van Meel, who, as an employee with a radiation certificate, assisted me with the measurements with the DE-XRT scanner at the Stevin lab, TU Delft, as well as to Ron Penners, who was the supervisor of the experiment.
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Chapter 1 Introduction

Like any other industry, the mining industry is exposed to changes in society and the world market. One of the greatest challenges of today is meeting the increasing demand in the upcoming years. New discoveries of ore bodies still take place nowadays; however they are too small in number to meet the increasing amount of metals which are required worldwide. Another concern is the fact that most new discoveries are in areas which are difficult to access, which leads to an increase in mining and transportation costs.

In general the industry faces a problem of decreasing grades, increasing waste to ore ratios and increasing mining and mineral processing costs. Many solutions to these problems have been proposed, but one of the most realistic of them is the use of improved technology. Sensor based sorting operations have the potential to become a major part of the solution to today’s difficulties. They are capable of detecting properties of single particles and can be used to separate particles when connected to appropriate devices.

Many sensor based sorting techniques are available nowadays, but in this project the focus is on DE-XRT (Dual-Energy X-ray technology). The investigated ores the porphyry copper ores from the Los-Broncos mine in Chile. The main question is if DE-XRT technology is a suitable tool to classify for ore and waste material based on copper grade. In other words: Is there a correlation between the DE-XRT data and the copper grades?

Other topics of interest are:

- How does DE-XRT work?
- What are the advantages and disadvantages of DE-XRT compared to other sensor-based sorting techniques?
- What is the effect of applying different thresholds on the reliability of the DE-XRT data?
- Can DE-XRT add value to XRF and/or NIR spectroscopy in terms of distinguishing between ore and waste material?

This report will contain a theoretical part, where sensor based sorting, DE-XRT, XRF, NIR and porphyry copper deposits are discussed. This is followed by a chapter regarding measurement technique, a chapter about the results and some analysis on them and finally a conclusion and discussion based on the obtained results.
Chapter 2 Theory

2.1. Introduction to ore sorting

2.1.1 History and importance of sensor based sorting

The oldest process in ore sorting is hand-picking, however it is not so much used anymore, and it is still applied in small scale mining. On the industrial scale it is sometimes used for the pre-concentration of rock salt or hard coal, but the amount of operations for which it is used is decreasing.

Sensor based sorting machines have been developed and applied since the 1950s, with a wide amount of sorting criteria. For example electric conductivity and radioactivity can be used criteria. Twenty years ago, x-ray fluorescence sorters were introduced in the last concentration step in diamond processing. Parallel to this, photodiode sorters were developed. The major drawback of these devices is that they have limited throughputs and the fact that they can only handle feed sizes below 20 mm.

The combination of modern processing techniques and high resolution digital scan line cameras led to the development of optical sorters, mostly for recycling operations. These are capable of the high throughputs and coarse sizes up to 250 m. As a result of this, they are also interesting to use in other mineral processing applications. As a consequence of the current advances in sensor, computing and material handling technologies, sensor-based sorters have the potential to establish themselves as a standard unit-process in mineral processing. Especially when combinations of sensors are used, minerals that could not be separated with the conventional separation techniques, for example as a result of overlapping densities, can now be separated as well.

The main distinction between sensor based sorting and the classical separation unit processes is that single particle sensor-based sorting is the only process with a decoupling of the material properties from the mechanical separation. The principle is that a certain property is measured, the measurements which are obtained are analysed by a processing unit, from the analysis a positive/negative decision is derived, this actuates the mechanical separation (Riedel and Wotruba, n.d.)

2.1.2 Sensor based sorting and the mining industry

The mining industry is exposed to changes in society and the market over time, the main challenge is to find a way to adapt to changes. One of the greatest concerns nowadays is the increasing demand. New ore body discoveries have taken place, but not in a rate which is enough to meet the increasing demand. Moreover, most of the recent discoveries are in areas which are difficult to access and are further away from the surface. This leads to increased mining and transportation costs. All in all, there are a few major problems for the industry: lower grades, deeper mines and decreasing ore to waste ratios, as a result of this, costs are rising.
Different solutions are available to this problem, however, the following options have been investigated over the past years:

- Up scaling of mines, resulting in ‘mega mines’ at low grades.
- Making a trade-off: metal extraction through huge transport or in-situ-leaching.
- Re-definition of ‘ore’ and ‘waste’ through improved technology

The first option does not solve the whole problem. In reality engineers face long-term projects with huge CAPEX, resulting in high requirements considering the planning of the entire problems. Companies can hardly afford mistakes from the beginning on. The problem with massive leaching is that it cannot be used in every case. For example, minerals with overlapping density cannot be separated properly.

Maximizing the usage of improved technology can be the key to the solution of the problem of lower grades, lower ore/waste ratios and pressure on the costs. This implies a more careful and critical approach to the mining and processing activities. For example, better understanding of the ore body variability is needed, in terms of mineralization, textures, structure and alteration. Also improvements in recycling contribute to this, as well as an optimised process flow from the resource to the market. This means that existing operations are improved if possible, and the knowledge gained from this is used by the design of new unit operations.

Sensor operations are an important part of the improved technology plan, because of their capability to identify material properties, and use this to separate materials if connected to the appropriate devices. Considering the development of the sensors, there are some important points. For example the definition of sensor combinations of specific tasks, the development of sensors were required and the demonstration of economic and practical benefits. Many different techniques are available nowadays, for example infrared, X-rays (XRF, XRD), electromagnetic, lasers, Mossbauer and optical.

The sensor operation of interest for this project is the sensor based sorting process. The development of this technique of sorting operation is important due to the large costs associated with mineral processing (about 10 times larger than the costs of mining). It may be clear that anything which reduces the costs of the processing is of interest to the industry. Innovative techniques as well as improved efficiencies can contribute to this. As mentioned before, the most important thing to keep in mind is that only the economically valuable material has to be produced (Buxton, 2012)

### 2.1.3 Description of the process

Before any sorting operation can take place, it is essential that the material conditioning is done properly. This prepares the material to be properly detected by the sensor arrangement. The next step is the particle isolation and presentation to the sensors. Because this is a single particle method, each particle has to be presented separately with enough distance with respect to neighbouring particles. The recognition and detection of the characteristics is achieved with a source of electromagnetic radiation and combination of sensors, which detect reflection or transmissions of the radiation source. The data of the
sensors is sent to a central processing unit where it is electronically analysed and measurements are linked to each element. From pre-set material characteristics, an accept/reject decision is derived and the mechanical separation device is activated.

Several parameters influence the material conditioning. Firstly, it depends on the material to be sorted. Secondly further processes downstream are important. These processes include requirements for particle isolation, sensor type and mechanical separation technique. The most important process is to screen the material in order to obtain a size ratio of below three. Another important process is the cleaning of the material by washing/scrubbing or de-dusting, processes which heavily depend on the material properties. Therefore, it is difficult to give a general explanation of them.

The purpose of the isolation process is to present single particles, without any overlapping, but in the most efficient way in terms of throughput. The principle is that the particles are both accelerated and spread out on a larger working width than in the previous conveying mode. Due to these changes, particles are being drawn apart from their neighboring particles. Isolation in the most efficient way means that the goal is to achieve a single particle layer with the densest surface possible, without particles touching each other and enough distance to each other allowing a selective rejection of each particle. The first step for the acceleration is in most cases a vibrating feeder. This device is limited to a maximum velocity of 1m/s. The advantage of it is, however, that it able to spread the material over any desired width.

The main acceleration step can be achieved with two methods: the usage of a flat conveyor or a sliding chute. Both methods have advantages as well as disadvantages. Therefore the preferred method depends on the material characteristics and sensor arrangement. Two methods are available matching the sensor and rejection capacities of the system, channeled and random feed. In a channeled feed the position of the particles along the working width is fixed. In a random feed presentation the particles are randomly distributed along the working width, their exact position has to be measured by the sensor arrangement.

The detection of the material properties of interest is achieved with a suitable sensor arrangement, which is, as explained before, dependent on the material and the type of material characteristics which have to be investigated. In many cases one sensor is sufficient. Sensors are only the first part of the detection process. Emissions in a certain part of the electromagnetic spectrum can only be measured when the material is exited by a source which emits radiation in the desired spectrum. Crucial in the process is the geometric arrangement of source, material and sorter; this often influences the success of a sorting operation, in the lab as well as in field applications.

After the material characteristics are seized by a sensor the data have to be processed. The aim of this is to obtain a particle by particle decision to reject or accept. Two concepts can be used for processing, however they are very different. The first possibility is the usage of direct coupling of single sensor with single discharge units. With this technique it is only possible to recognize and reject the area of the particle directly in front of the sensor. Each sensor in the arrangement actuates the rejecter directly linked to it. This implies that there is no possibility to analyze measurements from different directions in a statistical way and
derive a decision from that. Therefore this technique can only be applied in combination with a channeled feed presentation.

Figure 3.1 sensor based sorting operation. The example shown here is the OSX series of comex

The second concept is the parallel processing of the whole sensor line and flexible actuation of the rejecter mechanism. The central concept is that the information from each sensor in the arrangement is put together simultaneously to a coherent picture, which allows to identify singled particles. Then statistics are used to analyze all measurements for one particle and a decision is obtained from a pre-set thresholds particle by particle. The actuation of the separation mechanism is derived from the position and the size of the whole particle. In this process it is allowed to choose channeled feed as well as random feed.

The goal of the mechanical separation process is the exact rejection of single positively identified particles. The most important variables of the process are actuation velocity, force and resolution. These parameters are chosen based on material properties, operating conditions and particularly the contamination of the detection area. The three most used methods are air valves, water jets and mechanical flaps. The preferred method is the use of air valves, for their high actuation velocity and accuracy. With the exception of the mechanical flaps, the target is not to let particles fly into an air- or water flow. Instead, directed impulses are applied onto the particles passing by the rejection bar. The rejection bars can be arranged in different ways, according to the philosophy of the engineers. They can be aligned from under the product stream or from above. When a chute presentation is used, they are mostly aligned from under the stream. Both methods have advantages as well as disadvantages, which depend on material properties, valve contamination and the required rejection forces (Riedel and Wotruba, n.d.)
2.1.4 Parameters affecting throughput

Several parameters influence the throughput of the whole sorting process. Geometric properties, average particle weight, particle isolation efficiency and coverage, rejection speed and accuracy, rejection percentage and signal processing, speed and accuracy.

The area per unit time that can be scanned by a sensor arrangement is determined by working width and transport speed. The sides of a belt or a chute influence the isolation and the calming of the particles. Therefore a side factor has to introduce. This reduces the effective working width by a certain percentage.

The weight of the particle depends on the size range, the density and the shape factor of the material. When the average size and the shape factor are known, the volume can be calculated, when it is multiplied by the density an average particle weight is received. Because a theoretical shape factor is used there are a few uncertainties linked with it. These uncertainties can be eliminated by measuring the average particle weight for arbitrary size ranges and put them into the equation.

The particle isolation efficiency is a measure for the area which is attributed to each particle. Dividing the total area by the area per particle defines the coverage. To illustrate the coverage, the concept of the ‘bounding box’ is introduced. The bounding box factor is the ratio of the average distance between particles and the average particle size.

The rejection speed and accuracy depend on the resolution and speed of the mechanical separation units, the particle isolation efficiency as well as on the feed rate. It may be clear that the worst case scenario is a slow and inaccurate rejection unit along with inefficient particle isolation. The result of this poor performing units can result in the rejection of adjacent particles and the production of higher amounts of mass than identified by the sensor analyzes components. To counteract to this the effective sorting area has to be reduced, which effectively reduces the throughput. Generally, the resolution of the sensor and the rejection unit has to be fitted with the size range which has to be rejected.

The percentage of the material to be rejected has a major influence on the real throughput. At higher rejection rates, the particle isolation efficiency becomes increasingly important and influences recovery and product grade. In general, the ideal throughput calculation can be applied for rejection rates up to a maximum of 20 %. For higher rates, the effective throughput has to be lowered. The circumstances also influences the material fraction to be rejected (Riedel and Wotruba, n.d.)

2.1.5 New developments in Sensor-based sorting

At the moment, many color sorting machines have been used in the mineral industry, either to pre-sort recovered material or to enrich minerals of value. These machines produce acceptable to good results as long as the color differences correspond to the material differences. However, the problem is that for most of the possible applications of bulk
material sorting based on single particles, there is an insufficient or even absent relation between the color differences and the mineral composition. Therefore, new sensor types are required, which make use of properties like molecular structure, thermal conductivity and more.

One example of a new technique which could be useful in the mining and mineral processing industry is dual-energy x-ray transmission (DE-XRT) which is already used at airports for luggage inspections. With this technique, the material is exposed to x-ray radiation, and the material absorbs at least a part of it. The amount of absorption is determined by atom number, density and thickness. Because low-energy as well as high-energy x-rays are used, the material properties can be determined independently of the thickness (Harbeck and Kroog, 2008).

Recently, many studies have been performed regarding the DE-XRT technology. Harley Stydom looked at the possibility of removing torbanite of coal ore for his MSc thesis at the University of Witwatersrand, South-Africa. The conclusion from his report is that clear distinctions between coal, torbanite and shale fractions can be observed by using this technique. As a result of this, the caloric value of the product could be improved significantly and ash content could be lowered as well (Strydom, 2010).

Sensor based sorting techniques like (DE)-XRT, XRF (x-ray fluorescence spectroscopy) and NIR (near-infrared spectroscopy) will be discussed in the upcoming paragraphs.

2.2. Sensor based sorting techniques: XRF, NIR and XRT

2.2.1. Introduction and basic theory of XRF

The X-ray fluorescence technique can be used in the mining industry for purposes of managing exploration quality control and mineral processing control. It is a simple and efficient method of quantitative as well qualitative analysis. The technique has considerably lower costs and higher speed when compared to conventional chemical methods. With the use of this technique, the element composition of minerals can be determined quickly and non-destructively.

Elements can be analyzed simultaneously by measuring the emission of characteristic x-rays. Firstly, emitted x-ray hits the atoms of the sample. The x-rays collide with electrons in the K,L or M-shells. This results in the removal of these electrons from their respective atomic orbits. Secondly, electrons of ‘higher’ shells fill up the vacancies and emit characteristic x-rays. The energy of these x-rays represents the energy difference between the two shells of electrons. X-rays are identical when electrons of the same atom move between shells (Beckhoff et al., 2006).
2.2.2 Components of the XRF-analyzer

The XRF analyzer is composed of an x-ray tube, a detector, a multi-channel analyzer and a computer. The detector detects fluorescent x-rays from the sample and converts them into voltage pulses. The multi-channel analyzer aims to create a spectrum of characteristic x-rays. In order to do this, the voltage pulses are matched with energy values, therefore taking the amount of times an energy value occurs into account. Finally, the computer edits the data received from the energy spectrum by using a few factors and calculates the chemical composition of the sample based on the modified energy spectrum (Tong, 2009).

2.2.3 XRF-sorting and its applications

Apart from being useful for chemical composition analysis, XRF also provide a sensing method for automatic ore sorting and preconcentration. A few studies have been done on XRF ore sorting. The work consisted of renewing a XRF-ore sorter from RADOS to use for the upgrading of manganese ore. One of the conclusions which could be drawn is the fact that the suitability from a specific ore to XRF sorting technology depends on the availability of particles with varied grades.
The XRF sorting uses the same technology as the XRF analyzer. Rocks are separated based on chemical compositions through the measurement of the concentrations of different elements at the rock surface. A pre-set threshold used to determine if particles respond to the ore of waste fraction (Beckhoff et al., 2006).

2.2.4 NIR Spectroscopy

Nowadays NIR is used mostly as a geological exploration tool for remote sensing and for the laboratory identification of pure minerals. The separation of minerals in technical processes by using sensor technologies is an application which is relatively new. With NIR spectroscopy a ‘fingerprint’ from the sample is obtained, directly related to the mineral composition. The fingerprint is the spectral response of the mineral to the emitted NIR radiation. A part of the radiation is absorbed by the mineral, resulting in a spectrum with absorption features.

One of the most common features to be seen in the NIR-spectra of molecules is caused by the unfilled electron shells of transition elements (Ni,Cr,Co,etc.) and is known as the crystal field effect. The crystal field depends on the crystal structure (spatial arrangement of elements) and therefore varies from mineral to mineral. This implies that the same ion can cause different absorptions, creating the possibility to identify specific minerals with NIR-spectroscopy.

Minerals show absorption features between 1300 and 2550 nm, spectral responses of heterogeneous material are more complicated. Mixed spectra are a result of diluted rocks, contact zones between different rock types, and the presence of water in the material. During the detection of the response, these mixed spectra can also be the result of a too low spectral resolution. This is a risk for the observation of small heterogeneous samples. The combination of NIR spectroscopy and object recognition creates to possibility to make decisions on single particles based on the statistical features on the classification results of the specific particles. For inhomogeneous particles object recognition improves the overall classification result. Also material rates can be calculated based on the classification, which allows determining the chemical composition of samples (Robben et al., n.d.)

2.2.5 The x-ray transmission theory

When materials are exposed to x-rays, they will absorb part of the radiation. The reduction of the initial x-ray intensity is called transmission damping. The amount of x-ray which is transmitted through materials depends on the density of the material. As a rule of thumb, the denser the material the more absorption and the less transmission will occur. Transmission damping depends on density and thickness of the material according to Lambert’s law, which will be explained later on when the topic Dual Energy x-ray transmission (DE-XRT) is discussed. DE-XRT is the kind of XRT technology to which the most
attention is paid in this report, in the coming sections; it will be in terms of technique, applications and new developments.

2.2.6 Technical principles of the XRT-scanner/sorting program

For this particular project, Dual Energy X-ray transmission (DE-XRT) is used in order to distinguish low and high copper grades of the different samples. DE-XRT is most known for its use in airport luggage scanners. The sensor emits X-rays, which are transmitted through the material. However, energy is partly absorbed by the material according to the law of Lambert-Beer:

\[ I_{\text{det}} = I_0 e^{-\mu \rho x} \]

- \( I_{\text{det}} = \) detected intensity (-)
- \( I_0 = \) initial intensity (-)
- \( \mu = \) mass attenuation coefficient \((m^2/kg)\)
- \( \rho = \) material density \((kg/m^3)\)
- \( x = \) material thickness \((m)\)

In this context, the mass attenuation coefficient in the law of Lambert-Beer relates to the absorption of x-ray radiation by the wavelength of the radiation. This relationship depends mostly on the effective atomic number of the material. Effectively, the absorption of x-ray radiation by a certain material depends on atom number, density and thickness of the material. However, to use to principle of X-ray radiation in order to classify the material, one would like to leave the material thickness out of the equation. When material thickness is still taken into account, it will not be possible to distinguish a thin material with high x-ray absorption from a thick material with low x-ray absorption.

The key to the solution of this problem is the use of two different wavelengths or energy levels (dual-energy) of x-ray radiation, in combination with a normal XRT sensor. Hence, we now have two dimensionless detected energies \((I_1 = I_{\text{det}}, 1/I_0, 1\) and \(I_2 = I_{\text{det}}, 2/I_0, 2\)). When the law of lambert-Beer is used for both of them, the following result is obtained:

\[ \frac{I_1}{I_2} = e^{-\mu_1 \rho x}/e^{-\mu_2 \rho x} = e^{-(\mu_2 - \mu_1) \rho x} = (e^{\Delta \mu \rho})^x = C_m^x \]

In the equation listed above \(C_m\) is a constant that only depends on the material properties effective atomic number and density in combination with the two wavelengths that are chosen for the two energy levels of x-ray radiation. Therefore, the thickness of the material is left out of it. This allows to characterize material based on the material properties alone. The only condition for this is that the \(C_m\) of the two materials must be different.
When materials of different thicknesses are scanned with a DE-XRT sensor, a graph with different transmission curves of the material can be obtained. A transmission curve is a graphical representation of the transmission observed by the high- and low energy x-rays (y-axis) at various material thicknesses (x-axis). Transmission curves provide information on how the material thickness influences the detected x-ray radiations for both energy levels. When a transmission curve of a known material is used as a reference, the detected x-ray intensities for an unknown material can be evaluated independently from the material thickness.

One might ask how this principle works in practice, say when evaluating images made by a DE-XRT scanner. When using Tricolor images, R/G/B (red/green/blue) values are assigned to the measured pixels. In the program used for this report, green represents the results around the reference transmission curve (aluminum), blue represents measured results above this transmission curve, red represents results below this transmission curve.

2.2.7 Applications of DE-XRT technology

Several studies have been performed in order to find practical applications for the DE-XRT technology in the mining and mineral processing industry. At the technical university in Delft, the usage of the technology for the sorting of coal, minerals and secondary resources has been studied since 2000. Some interesting results were obtained, for example it was shown that the ash content of coal can be significantly lowered when using the technique. When comparing it to other automatic sorting techniques it has the advantage that sorting is not influenced by moisture fluctuations, surface dirt, and shape or size effects. When looking at dry physical separation techniques, it can be concluded DE-XRT shows better efficiency and is suitable for a wider size range.

In 2005, CommoDas GmbH introduced a new DE-XRT sorter on the market. Due to the relatively high sensor resolution, effective width and conveying speed, this device allowed the automatic sorting of larger volumes of coal (usually around 5-25t/h of coal per machine). In comparison to a conventional wash plant, the device is compact and can be used as mobile equipment. Wim Kuilman from the TU Delft investigated the efficiency of this type of sorter on a large number of different copper samples (Kuilman, 2006).

2.3 Porphyry copper ore

2.3.1 Introduction

The investigated ores in this project are porphyry copper ores from Chile. In order to analyze the ore and understand the obtained results regarding the average atom number in relation
to the iron and copper grades, it is essential to gain some background knowledge regarding the geology and abundance of these deposits. This chapter aims to give a broad overview on first the class of ore deposits to which the porphyry copper ore deposits belong, the hydrothermal ore deposits. Then the porphyry copper ore deposits themselves are discussed in terms of geology and mineralogy, finally the relevance of these deposits in relation to copper mining projects is analyzed.

2.3.2 Hydrothermal ore deposits

Hydrothermal ore deposits are a wide class of deposits, their genesis is related to hot aqueous solutions. The origin of these solutions however, is not related to a single process alone. In fact a wide range of processes have contributed to the genesis of the solutions like magmatic, diagenetic, meteoric and sea water related events. In many cases, solutions of different origin have mixed. The metals found in the resulting deposits may be constituents of the original solutions, but may also be leached from rock through which the solutions flowed.

Hydrothermal solutions vary in temperature from 50 to 650 degrees Celsius. Also a wide range in pH values can be observed, from acidic to near neutral. In most cases, metals are dissolved in the fluids as complexes of Cl\(^{-}\) and HS\(^{-}\), in minor amounts; they may also be dissolved as complexes of H\(_2\)S and NH\(_3\). In general, ammonia concentrations are quite low, and chloride species dominate over the others. In general, there are five processes which lead to the crystallization of fluids: rock-fluid interaction, redox changes, adiabatic expansion, cooling and saturation with respect to a compound (Voncken and Wolf, 2011).

2.3.3 Porphyry copper and molybdenum deposits

This group of deposits is related to intrusions that have risen to a high level in the crust. The intrusions are of the sub volcanic type. Depths vary from one to four kilometers at the point where mineralization occurs. They are found on the continental side of subduction zones. As a result of the small depth of formation, most preserved deposits are cretaceous or younger of age. Aqueous fluids exsolved from the cooling magma accumulate in the apical region. Under the regime of retrograde boiling they escape by hydro fracturing of the intrusion roof. The crystallization of the remaining silicate is accelerated and porphyritic granite is produced. The magmatic hydrothermal fluids contain major elements and trace metals, under influence of these solutions metasomatism of the surrounding rocks occurs. Their soluble elements like copper, molybdenum and sulphur precipitate as sulfides, chalcopyrite (CuFeS\(_2\)) and molybdenite (MoS\(_2\)).

The hydro fractures seal as a consequence of metasomatic mineral formation and sulfide crystallization. As a result the trapped fluids experience retrograde boiling. They break out again by hydro fracturing. The repetition of this process produces a stock work of sulfide vein lets and disseminated sulfides. As the system cools, convecting groundwater will flow along with the rock material; this water produces a hydrothermal alteration system. First the water enters the distal zones affected by the magmatic hydrothermal solutions. This leads to the formation of a propylitic zone, where biotite is converted to chloride. Later, argillic
overprinting of the outer zones of the potassic alternation core is caused by the fluids. In this zone biotite is converted into clay minerals. Finally it causes overprinting of the outer zones of the potassic alternation core; here feldspars are converted into sericite and quartz. These solutions also remobilize, redistribute and enrich the copper sulfides. The recognition of these zones is essential for exploration purposes.

Figure 3.3 the different mineralogical regions in a porphyry copper system

Porphyry copper deposit locations are strongly linked to orogenic belts. This association is clearest in the circum-pacific Mesozoic to Cenozoic deposits but is also seen in North American, Australian and Soviet Paleozoic deposits within the orogenic belts. Porphyry deposits are found in two main setting within the orogenic belts, in the island arcs and the continental margins. Deposits of Cenozoic and Mesozoic age are predominant, from the Paleozoic and Precambrian age however, only a few deposits with characteristics similar to porphyry coppers have been found. Deformation and metamorphism processes obscure the primary features of the older deposits. As a result of this it is more difficult to recognize them (Voncken and Wolf, 2011).

2.3.4 Porphyry copper ore from the Los Broncos mine in Chile

After a brief introduction to hydrothermal ore deposits and porphyry copper types in particular, the focus will be on the porphyry copper deposit in Chile where the investigated samples come from. All of them are collected at the Los Broncos deposit, which is located on
the west side of the Andes in central Chile, situated about 69 kilometers from Santiago, the
capital of the country. The Rio Blanco mining company currently exploits the north central
part of this porphyry deposit. The company has started operating a mining operation on a
large copper-bearing breccia deposit two kilometers south of the present mine, as well.

The Los Broncos-Rio Blanco deposit was formed on the east side of the San Francisco
batholith. This intrusion is predominantly peraluminious and has a calc-alkaline composition.
The batholith has been formed between the early Miocene and the late Miocene, a period of
about 11.5 million years. The porphyry copper mineralization, alterNation and copper
tourmaline breccias were formed over a time span of 2.5 million years, between 7.4 and 4.9
million years ago. A second important geological event in this area of interest is the eruption
of the diatreme at La Copa, which removed a large portion of the northern part of the
porphyry copper system, which provided the last evidence of magmatic activity in the
region. The diatreme erupted between 4.9 and 3.9 million years ago.

The prebreccia porphyry system contains propylitic, sericitic, and potassic alteration. A
specific property of this system is the replacement of mafic minerals by specularite and/or
tourmaline in the propylitic zone. Copper-iron-molybdenum mineralization is abundant
within this system in an area of about 12 km². Los Broncos is composed of at least seven
different copper containing tourmaline breccias that from one large kidney shaped body,
which is about 2 km long and 0.7 km wide. The breccia body can be observed at the surface
at different spots between 3450 and 4150 meter attitude. The different breccias can be
recognized by their specific characteristics such as locations, matrices, shapes and degrees of
alteration. Most of the breccias are monolithic, but also bilithic and heterolithic types are
present. Most of the clast consists of quartz monozite or andesite. Some of them also
contain minor amounts of quartz latite porphyry, monazite and vein quartz. The breccias
matrices contain variable amounts of quartz, tourmaline, specularite, anhydrite, pyrite,
chalcopyrite, bornite, molybdenite, secrite, and chlorite.

The nomenclature for the different breccias is, in order of decreasing age: Ghost, central,
Western, Infiernillo, Anhydryte, Fine gray and Donoso. The contrast between the breccias
and the surrounding rock types, mostly intrusive rocks and andesites, is sharp. Within the
structure, the breccia contrast is well defined on some places. In most cases however,
gradational contacts can be observed. The breccias at Los Broncos are interpreted as being
placed explosively; thereafter they collapsed due to the pressure release of hydrothermal
fluids.

The primary mineralisation is found in the Donoso breccia. Ever since the start of the mining
activity back in 1864 it has been the center of the exploitation. Due to the coarse and
irregular characteristics of the sulfides in the matrix, chalcopyrite and pyrite are generally
distributed in irregular shells. In any of these shells, one of the three minerals is clearly
dominant in abundance. This phenomenon has been observed at the 3670 meter open-pit
operating level. The transitions between the shells are sharp. In vertically and laterally
neighboring parts of the subsurface, semi elliptical shaped shells of alternating high and low
copper grades have been found. Secondary enrichment increased the primary grades in the
southern part of the Los Broncos breccia complex and in a large part of the surrounding
porphyry copper system. The degree and depth of the enrichment are strongly related to the
breccia and fracture permeabilities. At some regions the enrichment extends to about 500 meters in depth. The shape and depth of the enrichment suggest that it is related to the present groundwater regime and still active (Warnaars et al., n.d.)
Chapter 3 Measurements

All the required measurements have been performed in the Stevin lab at the faculty of civil engineering and geosciences of the TU Delft. The device which was used is a DE-XRT scanner at the lab, which was previously used to scan luggage at airports. This scanner is the model APS system of the brand vivid technologies. The objective is to scan 58 porphyry copper samples from the Los Broncos mine in Chile, in order to derive information regarding the copper grades of these samples. Scanning has been performed with the help of Joost van Meel of the image analysis section of the TU Delft; the supervisor of the instrument is Ron Penners. The underlying theory behind the DE-XRT measurements is discussed in a comprehensive way in the theoretical part of the report; therefore this chapter will focus mainly on giving a brief description of the measurements.

The samples were scanned in batches of four; each batch was scanned two times. This is done for two reasons. First of all, having two results for each sample will make the results more accurate, also the probability of significant measurement errors decreases. Secondly, the particles are scanned in a different orientation at the second measurement. Considerably different results in the two measurements of the same sample could indicate that the x-rays are not able to penetrate through the whole sample. This would give an argument to cut the samples in half and perform a second measurement section.

The output of the scanning device consists of two images: a low energy and a high energy image. To process these raw data, in order to get numerical data, these raw files have to be processed. For this reason the TU Delft developed sort MFC application. This program combines the information of the two images to obtain information on several properties for each single particle; the focus in this report however is only on effective atomic number and the standard deviation of this number. In order to do this, the particles are segmented by using a certain threshold. This threshold (which can be seen as a cut-off) is based on the detected number of counts which are directly related to absorption. The counts are dependent on atom number, density and particle thickness. As a result of applying the boundaries, a part of the particle will not be analyzed. In most cases the areas which are left out will be at the boundaries of the particle, because of the low particle thickness in that region.

The final output is an excel file with data arranged per scanned particle. This data is analyzed in order to obtain graphs and to draw conclusions.
Chapter 4 Results

4.1 Effective atom number

From the obtained excel files after processing the data, the effective atom number and its standard deviation are the parameters of interest. A higher effective atom number could be an indication of a higher metal content, due to the higher density and atom number of metals compared to the other rock constituents.

Four different thresholds are used at the processing stage: 15, 100, 250 and 500 counts (minimum count rate, everything below this values is set to zero) in order to find a good balance between leaving irrelevant information and not leaving out parts of the sample which could contain ore. To illustrate the results, histograms with different thresholds are obtained with the effective atom number, the standard deviation and the difference between the two measurements on the same sample.

Figure 4.1 distribution of $Z_{\text{eff}}$ for a threshold of 15
Figure 4.2 distribution of $Z_{\text{eff}}$ for a threshold of 100

Figure 4.3 distribution of $Z_{\text{eff}}$ for a threshold of 250

Figure 4.4 distribution of $Z_{\text{eff}}$ for a threshold of 500
Figure 4.4 distribution of $Z_{\text{eff}}$ for a threshold of 500

Figure 4.5 distribution of the standard deviation of $Z_{\text{eff}}$ for a threshold of 15

Figure 4.6 distribution of the standard deviation of $Z_{\text{eff}}$ for a threshold of 100
Figure 4.7 distribution of the standard deviation of $Z_{eff}$ for a threshold of 250

Figure 4.8 distribution of the standard deviation of $Z_{eff}$ for a threshold of 500

Figure 4.9 distributions of the differences between the two measurements in different directions for a threshold of 15
Figure 4.10 distributions of the differences between the two measurements in different directions for a threshold of 100

Figure 4.11 distributions of the differences between the two measurements in different directions for a threshold of 250

Distribution of difference first/second measurement $Z_{eff}$ 500
From the graphs a few conclusions can be drawn. First of all it is observed that increasing the threshold decreases the range of observed values of \( Z_{\text{eff}} \) (abbreviation for effective atom number), also increasing the threshold leads to a decrease in the standard deviation for \( Z_{\text{eff}} \). These results can be explained by the fact that increasing the threshold removes areas with a low count, in many cases this is related to a low atom number. Leaving out low atom numbers leads to an increase in the effective atom number.

The most interesting result is the fact that the difference between the two measurements decreases considerably when increasing the threshold. This difference implies that the results obtained with threshold 500 are more reliable. This is because of the small difference in results for \( Z_{\text{eff}} \) compared to the average value of \( Z_{\text{eff}} \) (average \( Z_{\text{eff}} \) 13.08, average difference 0.26). When comparing it to the threshold 15 set (average 12.77, average difference 1.03) is clearly in favor of the threshold 500 data. Based on this information further analyses will be done on the ‘threshold 500 data’.

### 4.2 Comparison with the XRF results

One of the main objectives of this study is to determine if DE-XRT would be a suitable tool to separate ore and waste based on the copper grade. Therefore, the main question is: is there a relationship between the measured \( Z_{\text{eff}} \) and the copper and/or iron grades? In order to answer this question, the data on \( Z_{\text{eff}} \) are compared with data on the same sample set with XRF (x-ray fluorescence) spectroscopy.

The geochemistry data consist of two tables. One of them shows which elements are detected by XRF in each sample. The second one shows the detected abundance per element and the standard deviation of the measurements. With this information a theoretical \( Z_{\text{eff}} \) can be calculated which is in fact the summation of the abundance (ratio volume element/total volume) multiplied with the atom number for every element. In order to display this graphically, a histogram which shows the distribution differences in theoretical and measured \( Z_{\text{eff}} \), as well as a scatterplot with an fitted trend line and Rsquared-value (measure for ‘quality’ of correlation between data sets) of the measured and theoretical \( Z_{\text{eff}} \) are made.
Based on these charts, there is a reasonable correlation between theory and measurement (R-squared value of 0.75 is quite good), but there is a considerable difference in results for $Z_{\text{eff}}$ between XRF and XRT (average value of differences is 1.44, more than 10% of most observed values of $Z_{\text{eff}}$, figure 4.13). One of the explanations for this could be a threshold which has a too high value, but r-squared plots with the lower threshold datasets showed lower R-squared values: 0.71 for 250, 0.59 for 100 and 0.47 for 15. This gives another argument to prefer the threshold of 500, although it is far from perfect.
The main object of interest, however, is the correlation between the Zeff and the copper and iron grades. High values of r squared would indicate that DE-XRT is an applicable tool to determine or a sample should be classified as ore or waste based on the grades. The best way to invest the relationship is again, creating a scatterplot, fitting a linear trend line and obtaining the r-squared value (computed by excel). Scatterplots of Zeff/Cu Zeff/Fe and Zeff/Cu+Fe are created.

![Figure 4.15 comparison between the Z_{eff} and the copper grade](image1)

![Figure 4.16 comparison between the Z_{eff} and the iron grade](image2)
The first thing to notice is that there is a very weak correlation between the $Z_{\text{eff}}$ and the copper grade. This seems like a drawback for the DE-XRT because copper in the metal of most economic significance the copper price is about 6900 usd/ton, iron price is about 115 usd/ton (LME, July 2013).

However, there is a reasonable correlation (0.71) between $Z_{\text{eff}}$ and iron, which increases when the copper and iron grades are added up and correlated with $Z_{\text{eff}}$ again. This suggests that there might still be some influence of the copper grade on $Z_{\text{eff}}$, which can possibly be used in order to define a cut-off for $Z_{\text{eff}}$ to separate ore from waste. However, one remark has to be made here. From the six copper containing minerals (chalcopyrite, bornite, chalcocite, covellite and digenite), chalcopyrite and bornite also contain iron in their chemical formula. From the petrographic data it can be seen that chalcopyrite is present in a lot of samples, and therefore the fact that copper and iron together give a better correlation with the $Z_{\text{eff}}$ can be explained, because in most samples there are minerals present in which they occur together. For the last part of the results, the scope will be on the comparison between NIR (near-infrared spectroscopy) data and the measured DE-XRT data to check if the DE-XRT technology could be useful to improve separation based on NIR.

### 4.3 Comparison with NIR data

The principles of NIR spectroscopy have been discussed in the theoretical part of the report; here the focus is mainly on comparing the NIR data with the measured DE-XRT data. The NIR data consist of a table where based on a few measurements the probability for a sample to be an ore is given. The data are compared graphically. The first graph shows the $Z_{\text{eff}}$ plotted...
against the Cu=Fe grades, ore and waste are classified based on copper grade (>0.4% Cu is ore, other samples classified as waste). The second graph shows the same plot, but now the classification ore/waste is made based on the probability for the NIR.

**Figure 4.18** Graphical representation of the positions of ore and waste samples in terms of the summed grade of copper and iron and the $Z_{eff}$. Classification for ore and waste is done based on copper grade.

**Figure 4.19** Graphical representation of the positions of ore and waste samples in terms of the summed grade of copper and iron and the $Z_{eff}$. Classification for ore and waste is done based NIR ore probability.
By taking a look at the graphs, one might notice that there is indeed some correlation between the Zeff and the ore probability in both graphs, although that relationship is somewhat stronger for the NIR. For the DE-XRT to add value to the NIR measurements, the focus is on samples which are identified as ore by NIR, but as waste by DE-XRT. In other words, is there an extra fraction which could be separated from the ore by using DE-XRT as well as NIR? When looking at the samples lower than the 12,5 Zeff line, most of the samples here are classified as ore by NIR, but as ore by the DE-XRT. That would suggest that applying a cut-off for Zeff<12,5 would increase the processing efficiency for this sample set.

In order to check if a cut-off of 12,5 for the Zeff is a relevant number, the average cumulative Cu% values from the XRF are plotted against the Zeff values. Positive slopes indicate an increase in the copper grade in a certain Zeff range. The main idea behind this plot is to check if a certain trend in the dataset can be observed, to use this as an argument to define a cut-off value for Zeff.

![average Cumulative Cu% vs Zeff](image)

*Figure 4.20 Graphical representation of the average cumulative copper grade (cumulative copper grade/cumulative amount of samples) versus the Zeff.*

A few properties of the graph are interesting, first of all a steep slope is noticed between 12-12,5 Zeff, after that a short dip, which is caused by one sample which is significantly below the cut-off grade. After that a global increasing trend can be observed from 12,5 to 14 Zeff. This proves that there is indeed a correlation between the effective atom number and the copper grade. The most reasonable choice for a cut off is below 12,5 because this is the last point where the average cumulative copper grade is around 0,4 at higher Zeff, it increases steadily till 14. When comparing this with the scatterplots for NIR and DE-XRT ore waste classification, the conclusion can be drawn that there are some samples which can be identified as waste based on DE-XRT, while they are classified as ore based on NIR alone. By checking this more specifically with the excel data, the conclusion is that an extra 12% of the
samples can be removed as being waste based on the threshold for $\text{Z}_{\text{eff}}<12.5$ which is a quite significant amount.

On the other hand, one has to be careful with drawing conclusions based on the graph above. The main drawback of this research is the limited dataset which was available, which consisted of a number of 58 copper samples. Also the DE XRT test have been performed only twice per sample, in different directions. These two directions however are not always the same, because of the irregular shape of the samples. For further investigation about the economic and technical relevance of adding DE XRT to for instance an NIR operation, more samples have to be tested in order to gain more reliable results. Also the measuring procedure has to be more standard, by means of a more accurate description of the directions measurement and eventually multiple measurements have to be applied in each direction.

Based on this graph, one could also suggest applying a cut off to 14 and above because of the nearly flat line which indicates low grades. The flat line however, is more a result of the low abundance of samples with a measured $\text{Z}_{\text{eff}}$ of 14 and higher than a result of low copper grades. Therefore, a cut-off value of 12.5 would be the most reasonable choice based on this data.
Chapter 5 conclusions & recommendations

DE-XRT is a sensor based sorting tool which is based on the principle of absorption of x-rays by a certain material. The difference in intensity between the emitted and received x-rays is a measure for the amount of absorption. The amount of absorption depends on the atom number, density and thickness of the material. The difference between DE-XRT and other X-ray techniques is the fact that DE-XRT makes use of x-rays of two different wavelengths or energy levels. By taking the ratio of the two intensities, the material thickness can be left out of the equation, so an analysis based on the density and atom number alone can be performed.

The main difference between XRT and XRF is that XRF is based on reflection and XRT on the transmission of waves. XRF can detect unique elements by their absorption spectra, XRT cannot prove the abundance of a certain element, but DE-XRT can be used to do an analysis on the effective atom number, which makes it a useful tool to investigate the metal content.

The application of higher thresholds to the DE-XRT data in the TU Delft in-house sort program leads to a decrease in variability in the effective atom numbers, standard deviations and differences between measurements in different directions. However, there is a limit to this, because of the loss of data, a threshold of 500 is chosen because it matches best to both criteria. There is a very weak correlation between copper and the Zeff(R-squared value 0.05), but a relatively strong correlation between copper plus iron and the Zeff (r-squared 0.78). This can be explained by the fact that copper and iron occur together in the most abundant ore mineral, chalcopyrite(CuFeS2).

When the scatterplot of the iron plus copper grade versus the Zeff is taken, groups of ore and waste samples can be defined. If this is done based on copper grade first and then based on ore probability according to NIR, it can be noticed that a group of samples with a relatively low Zeff is classified as waste based on the copper grade, but as ore when the classification is based on NIR. This suggests that there is a correlation between the Zeff and the copper grade firstly, and secondly that DE-XRT can add value to a NIR ore sorting operation, because an extra 12% of waste can be defined.

A plot of the average cumulative copper grade versus the Zeff shows that for a Zeff higher than about 12.5 the average cumulative copper grade increases and stays above the 0.4 cut-
off value, this suggests that a cut-off for Zeff<12.5 could be useful in order to separate ore from waste samples.

Despite the fact that some conclusions about the applicability of DE-XRT for use in the sorting of porphyry copper ore can be drawn in this report, a few critical remarks can be made. First of all, the available dataset of porphyry copper ore at the TU Delft is very limited, only 58 samples could be used for this project. Also the amount of measurements is limited, because each sample has only been measured twice by the DE-XRT scanner, each of the measurements is in a different direction. However, these directions are not fixed because of the large variability of shapes in the sample set.

For a further investigation I would recommend the use of a larger dataset, as well as performing the measurements in a more structured way. One could think of cutting all the samples in a standard, for example elongated and performing measurements in the long as well as in the short direction. These two improvements could lead to a significant decrease of variability in the data.
Chapter 6 list of References

- Strydom, H, 2010., The application of dual energy X-ray transmission sorting to the separation of coal from torbanite. Johannesburg: faculty of engineering and the built environment, University of Witwatersrand. P6, 64-65
| Particle # | Intensity | Area Shape | Zeff | SD Zeff Low | abs SD Low | Hi abs SD | Hi SHi abs SD | SHi Avg,Red | Avg,Green | Avg,Blue | 128 | 128 | 81 | 138 | 87 | 112 | 4 | 86 | 59.343.523 | 85 | 85 | 128 | 0.666667 | 0.144295 | 99.33 | 0.664063 | 1.000.000 | 1.505.882 | 68.448.021 | 5.406.676 | 0 | 196 | 2641 | 0.698538 |