

Manganese Recovery: Missouri River Nodules

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Abstract

This research experience involved the collection of ore samples from Chamberlin, South Dakota. These samples were crushed, floated, and analyzed for composition. Both, X-Ray Diffraction (XRD) and X-Ray Fluorescence (XRF) were used in determining the compositions of the samples. One of the main objectives was to create a suitable metallurgical process to concentrate the manganese (in this case rhodochrosite) in the ore. Of the experiments performed, flotation was found to be the most successful procedure to increase the concentration of Rhodochrosite.

1. Introduction

Considerable low-grade manganese deposits exist along the Missouri river in central South Dakota, primarily on Lower Brule Reservation Land. This ore has been investigated previously and generally found to be uneconomical (6, 8, 9). This conclusion was partially due to expected high extraction costs and a relative lack of demand. Currently, the United States is completely dependent on foreign sources of manganese. A recent National Research Council study indicated that the manganese supply restriction has a high impact and that the supply risk was above average.

Recently, the price of manganese has increased sufficiently that the mining, extraction and production of manganese may be profitable when coupled with newer technology. An additional bonus is the existence of a relatively nearby steel operation (Nucor Steel) in Norfolk, Nebraska which may be interested in utilizing this material.

2. Source Material

Previous investigations of the Missouri River manganese nodules have gone a considerable way towards characterizing the type and disposition of these nodules. The following quote describes the nodules characteristics.

“The nodules occur in distinct layers parallel to the bedding of the enclosing shale. The average nodule has the size and shape of a large potato. Nodules may be widely separated or so closely spaced as to form a nearly continuous pavement. The Bureau of Mines has recognized three types of concretions: (1) hard concretions having a hardness of 4.0 to 5.0 on Moh’s scale, which are the most abundant, (2) soft concretions that have a hardness of 2.5 to 3.5 and that may be soft throughout or may have a hard core and (3) still softer nodules that grade into shale and are as likely to have fractures going through a concretion as around it. Types 1 and 2 easily break free of the enclosing shale.

Fresh un-weathered concretions of the hard variety are medium gray to olive. Weathered nodules have a gray center surrounded by a rusty brown halo and a purplish-black outer crust. The soft varieties are ordinarily white to cream colored when fresh and light brown after weathering. The concretions are mostly carbonates of manganese, iron, calcium, and magnesium. The non-carbonate constituents are mainly silica and alumina, probably present in the form of clay. A typical nodule contains 14 to 17 percent manganese and 6 to 10 percent iron (3).”

Referring to Figure 1, an old mine that was located in the Chamberlain, SD area can be seen on the left. Figure 2 shows the Research Experience for Undergraduate (REU) students collecting samples from the same area.



Figure 1: Above are the remains of the old mine near Chamberlain, South Dakota.



Figure 2: Students from the Back to the Future Research Experience for Undergraduates (REU) collected samples from the area in which a mine and processing plant was operated in the 1930's and 40's (9).

The research group first examined nodules obtained by Mr. Terry Rasmussen of Nucor Steel from near the previous pilot plant. Figure 3 shows the X-Ray Diffraction (XRD) spectrum of this material which shows significant amounts of dolomite ($\text{CaMg}(\text{CO}_3)_2$), rhodochrosite (MnCO_3), and quartz (SiO_2).

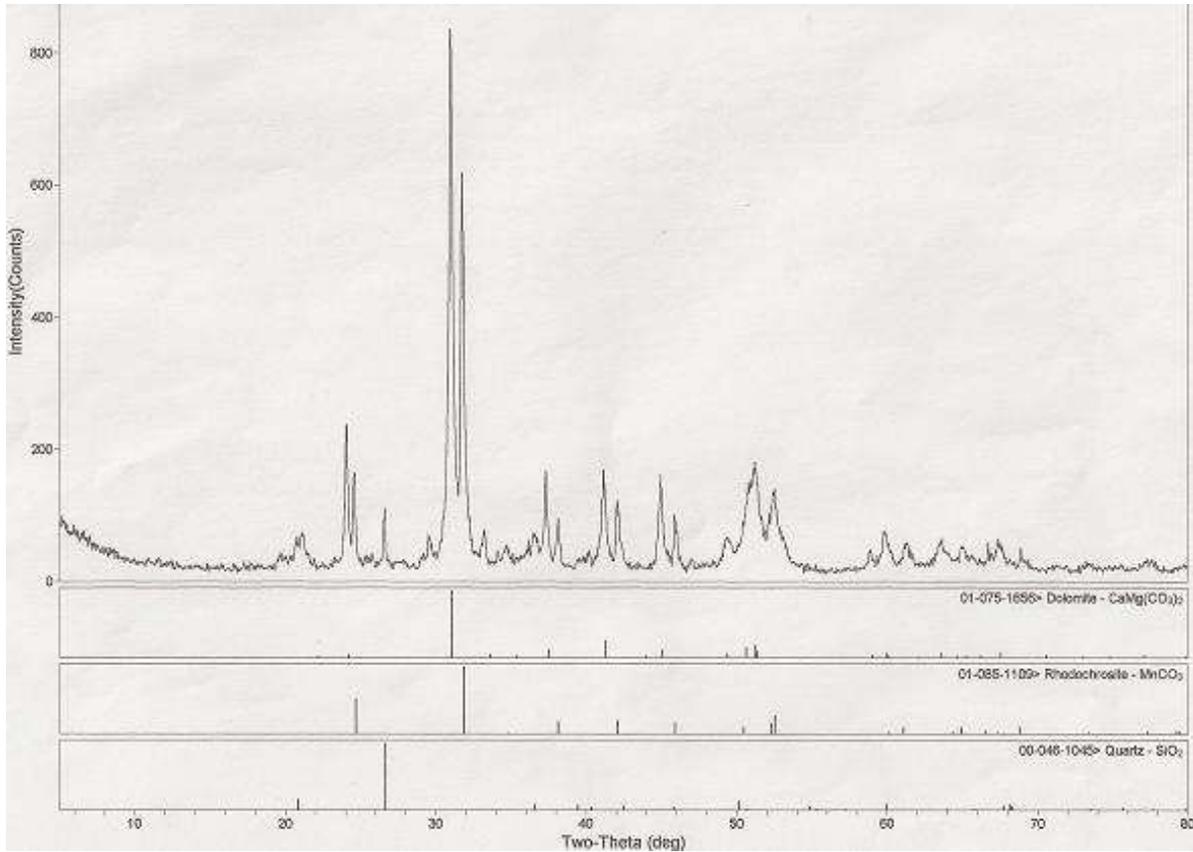


Figure 3: The raw material XRD results indicated that the composition contained 66.4% dolomite, 30.6% rhodochrosite, and 3.0% quartz

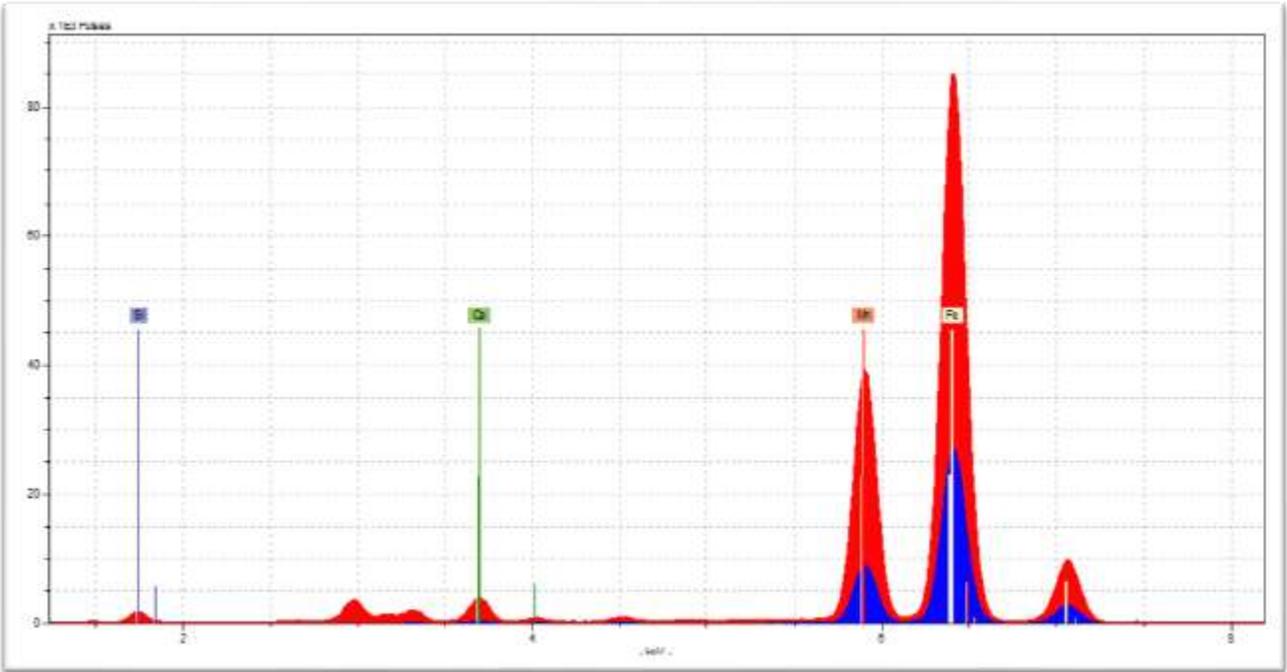


Figure 4: X-Ray Fluorescence (XRF) results from original soil sample.

Above (see Figure 4) are the X-Ray Fluorescence (XRF) results from the original soil sample. Unlike the XRD, this device recognized a large presence of iron. This is likely due to the fact that the iron compound is not in a crystalline form. Other than the occurrence of iron, the XRF results were almost identical to the XRD results.

3. Mining

In the 1970s, manganese sold for only pennies per pound. Prices have increased considerably and now the U.S. considers manganese a strategic metal. But in today's market, manganese is the fourth most consumed metal behind iron, aluminum, and copper. From the U.S. Geological Survey, Lisa Corathers, a manganese commodity specialist stated, "A continued supply of manganese material is vital to any defense effort as well as to maintenance and growth of an industrial economy." (2)

3.1 Manganese Economy

Manganese is an essential element in today's society. Its most significant impact is its use in the construction of steel, which accounts for 80-90 percent of manganese consumption. Other uses include paint pigments, dry cell and alkaline batteries, animal feed, glass production, fertilizers, and many medical and health applications. (1)

Manganese is critical to the steel production in the United States because of its unique properties when used for deoxidizing, sulfur-fixing, and alloying. One reason for increased demand is due to the newer methods for creating low-cost stainless steels that require larger than average amounts of manganese (1). In various alloys, nickel has been substituted for part to completely by manganese due to new heights in the price of nickel (4). Recent advancements in manganese steel alloys can consist of as much as 16% manganese with vital properties for wear-resistant application (4). This durable specialty steel is widely used in gyratory crusher plates, rail steel and cutting edges for earth-moving equipment (4). Manganese is important to the industrialized world and new uses for this element continue to emerge.

In 2008, the United States imported 571 thousand tons of manganese ore and 813 thousand tons of high manganese content alloys (1). Worldwide, miners removed 34 million tons of manganese ore in the year 2006, none of which came from American soil. When acquiring this strategic metal, the United States imports a large majority from only a handful of countries (see Figure 5). Over 80% of the world's known manganese resources are located in South Africa and the Ukraine (4). Ferromanganese is a manganese and iron alloy that accounts for a significant amount of the imported manganese and is fundamental for steel production. (see Figure 6). With no manganese substitute in the steel industry, it's very clear that the United States has a dependency on foreign suppliers for this element.

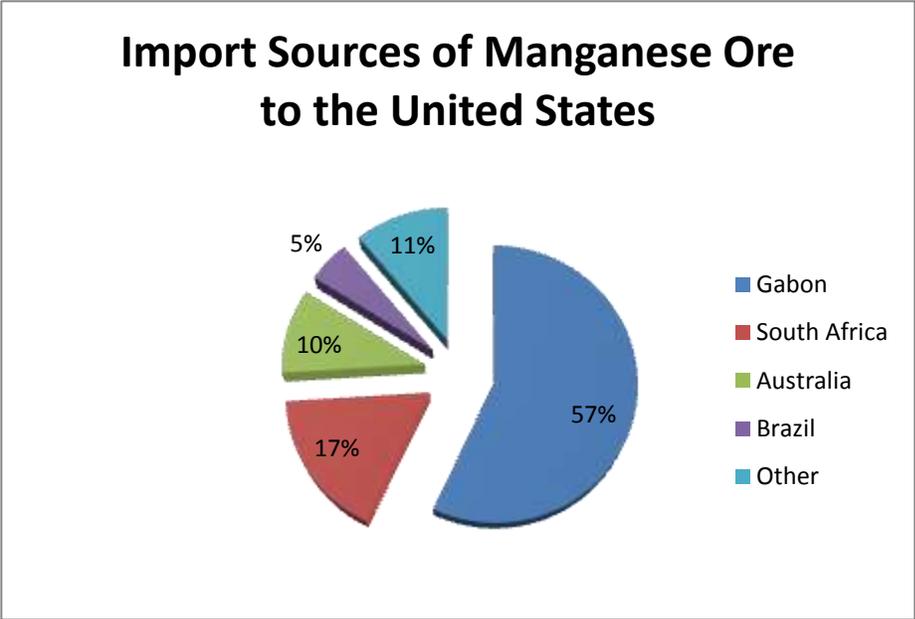


Figure 5: Import Sources of Manganese Ore to the United States (1)

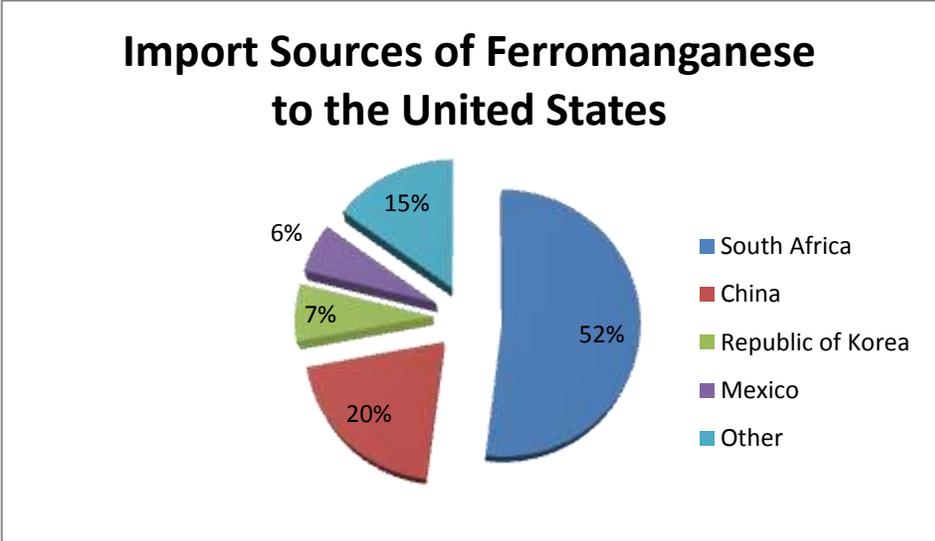


Figure 6: Important Sources of Ferromanganese to the United States (1)

3.2 Manganese Value

It has become clear that the price for manganese ore has a direct correlation with production prices in the steel industry. Using the graph below (see Figure 7), notice that the

price increase directly correlates to demanding times or a prosperous economy of the developed nations. The United States is fighting multiple wars which are creating a time of great demand. The price for manganese has reached considerable highs, and a local source in the United States is a great opportunity to minimize the exportation of wealth and for the creation of new American jobs.

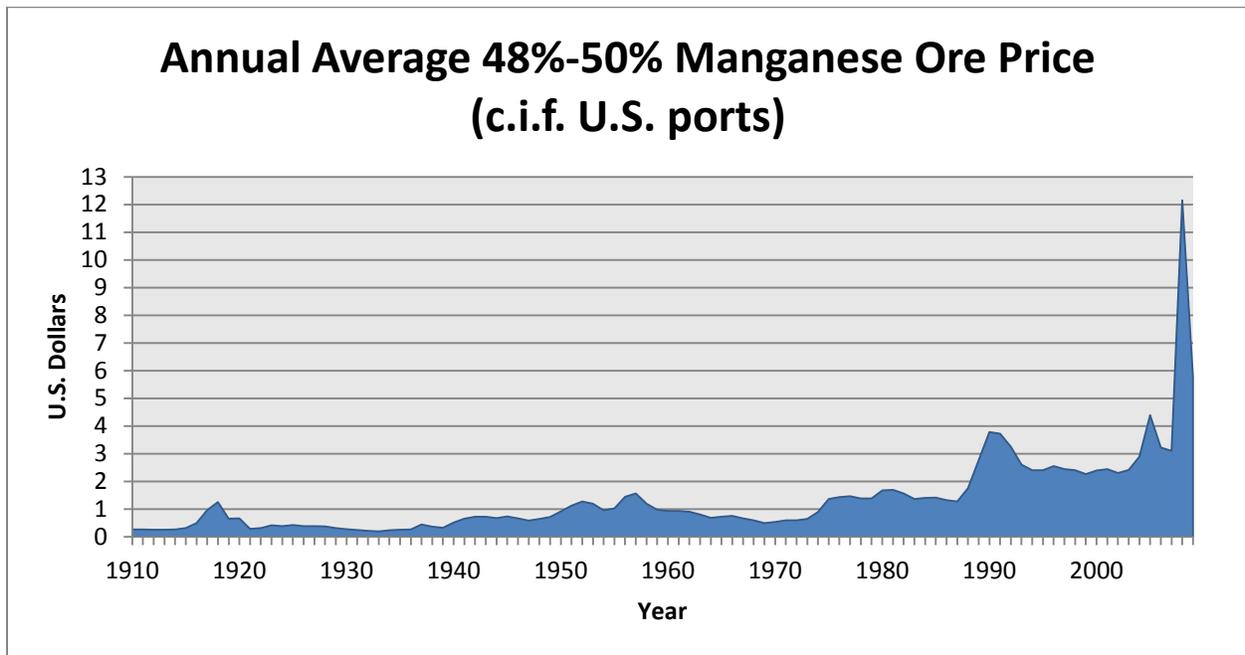


Figure 7: Price per metric ton over the last century.

Early in the last century, World War I put a strenuous strain on the world's production. Many nations, including the United States, stressed high output manufacturing of steels for this demanding time. With such a demand on the materials, prices were on the rise to a record yearly average high of 1.25 United States dollars (USD) per ten kilograms for manganese ore in 1918 (1).

The Great Depression was a devastating time for the economy, but as it came to an end, the recovery of the steel industry was in full swing as the Second World War (1939-1945) began. Once again, it is clear how a domino effect of a war leads to an increased steel output

and therefore a higher demand on steel components such as manganese. Only a half decade later there was a new record for the price of manganese as the Korean War created additional demand for steel production. Additionally, the creation of the European Coal and Steel Community in 1952 promoted an increase in steel manufacturing.

In the 1980s, two countries put such a demand on manganese that pushed prices to three consecutive all-time record highs. The Soviet Union was in the heart of the Cold War, and China was making significant imports of high-grade ore for their manufacturing. At that time, there were only three primary deposits supplying the world's major industries. This oligopoly of suppliers was overwhelmed by demand, resulting in a shortage of high-grade manganese ore. But in 1991 everything changed, as the dissolution of the Soviet. Demand decreased significantly, and prices slowly trended downwards (2).

In 2008, a perfect storm of factors pushed manganese to previously unimagined prices. The average price for manganese for the year was 12.15 USD per ten kilograms, almost four times the average price in 2007 (2). The dramatic increase in prices of oil dramatically affected ocean transportation costs for the shipping of manganese. China, India, and many other nations played crucial roles in increasing global demand as their developing steel industries prospered. The overall increase in demand spiked prices and inspired the development of new affordable resources of this mineral.

3.3 Desirable Manganese Form

Most steel companies use ferromanganese in the production of steel. Ferromanganese is used in steel making to alter the properties of steel. The manganese improves the tensile strength, workability, toughness, hardness and resistance to abrasion. According to Nucor representative Terry Rasmussen, Nucor Steel uses approximately 10,000 tons of manganese in their steel making processes every year.

4. Procedures

During the research period of the program, the research team developed a procedure to concentrate manganese. This procedure is explained in the following pages.

4.1 Crushing and Grinding

The methods of size reduction may be grouped in a number of ways, but since reduction occurs in stages, particle size provides the primary method of grouping. If the ore body is a massive one, mining is the first stage of size reduction and is generally carried out with explosives, although mechanical means may be used on softer ores. The term crushing is applied to subsequent size reductions down to about 25 mm, with finer reductions considered to be grinding. Both crushing and grinding can be further subdivided into primary, secondary, tertiary, and sometimes even quaternary, stages. Because these stages relate to the machinery used, the boundaries are not rigid, and in any given operation not all grinding stages may be required. Grinding can be yet further subdivided by the type of mill, the type of grinding media, and whether the grinding is carried out wet or dry (7).

For the data collection, a jaw crusher and a double-roll crusher were used for the first four trials. The subsequent trials (five through nine) were crushed using a jaw crusher and a dry ball mill, which ran for fifteen minutes. The crushed material was then separated by size.

4.2 Size Distribution

For this work, several samples of 500 grams were prepared and placed in a nest of sieves ranging from 10 to 325 mesh. The stack of sieves was then placed into a mechanical shaker for fifteen minutes. After the fifteen minutes, the remaining particles on each sieve were measured to the nearest 0.1 gram. The weights were totaled, and percentages were calculated for each sieve to the nearest 0.1%. Data shows that the samples prepared separated

in a similar way using the rolling mill (see Figure 8). However consistent the rolling mill seemed, the ball mill produced much finer particles, but had a wider range of sizes as well (see Figure 9).

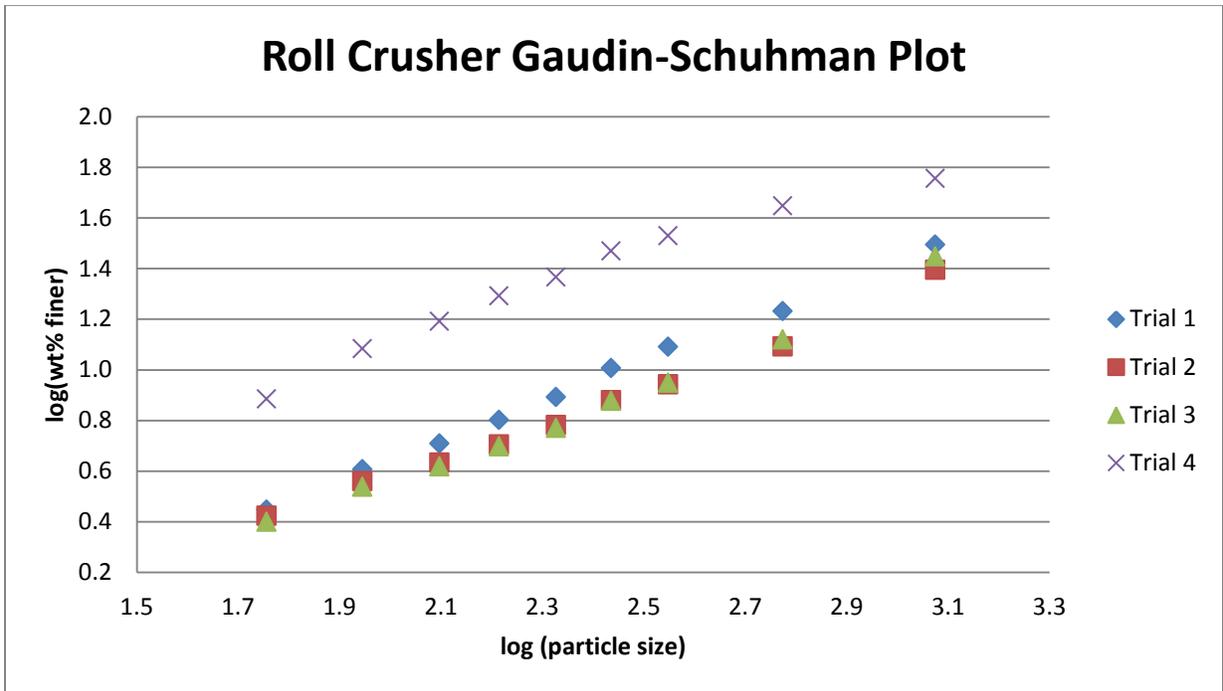


Figure 8: Roll Crusher size distribution data for four trials.

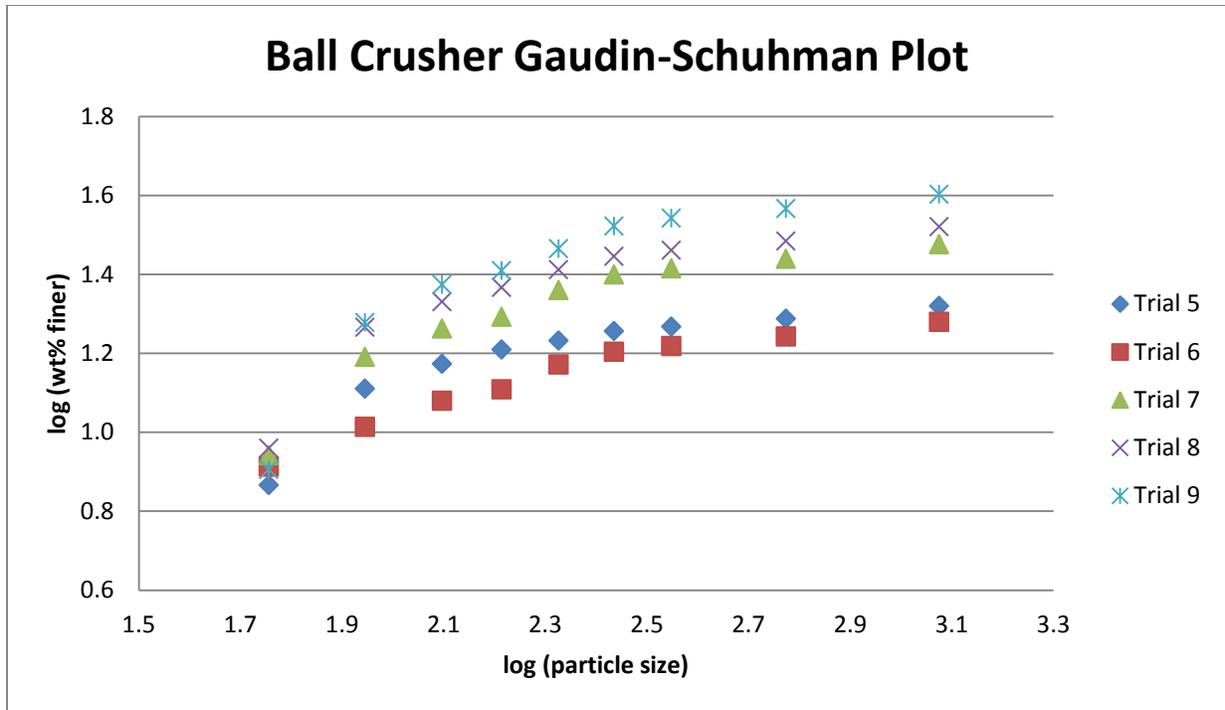


Figure 9: Ball crusher size distribution data for five trials.

4.3 Density Separation

Density separation uses the density differences of constituents in a mixture of materials to separate them. In general, the larger the density differences between the constituents, the easier and more feasible density separation techniques become. Also, density separation usually takes place in a fluid medium – namely water, air, or a particle filled fluid. Sometimes other fluids are used, but this process is usually more expensive, especially when used on an industrial scale. When calculating the settling velocities for the constituents in these fluid mediums, we applied the Stoke’s equation in some form. The settling velocities determine the time it takes for each constituent to settle. This is very important because the time it takes to separate the materials can be the deciding factor in whether the process is economically feasible.

There are some inherent advantages and disadvantages to using density separation as a method of separation. Density separation does not require any chemical reagents for success.

This increases safety and decreases cost in most cases. However, density separation is limited when trying to separate materials with similar densities. See Table 1 for a comparison of the constituent densities.

Table 1: Specific Gravity of Constituents

Constituent	Density (g/cm ³)
Dolomite (CaMg(CO ₃) ₂)	2.85
Rhodochrosite (MnCO ₃)	3.7
Quartz (SiO ₂)	2.66

To perform this test, the Wilfley Shaking Table was used. The Wilfley Shaking Table is a device used to concentrate particles in the intermediate range (10-200 mesh) of particles for ore and 3-100 mesh for coal. It is an oblong, shaking deck, typically 1.8-4.5 m wide, and the deck is partially covered with riffles that taper from right to left. The deck is gently sloped downward in the transverse direction. Feed enters at the upper right and flows over the riffled area, which is continually washed from a water trough along the upper edge of the deck. Heavy particles are concentrated behind the riffles and are transported by a bumping action to the left of the table where the flowing film concentration takes place; see Figure 10 (5).

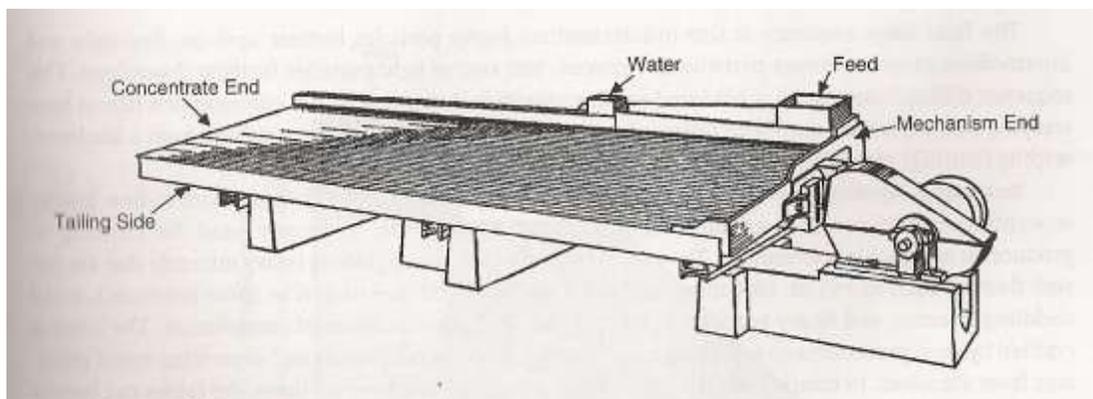


Figure 10: Wilfley Shaking Table (5).

4.3.1 X-Ray Diffraction (XRD) Results

After running experiments using the Wilfley Shaking Table, the lighter side of the table (the right side) was compared to the heavy side (the left side). See Figures 11 and 12 for the light and heavy side, respectively.

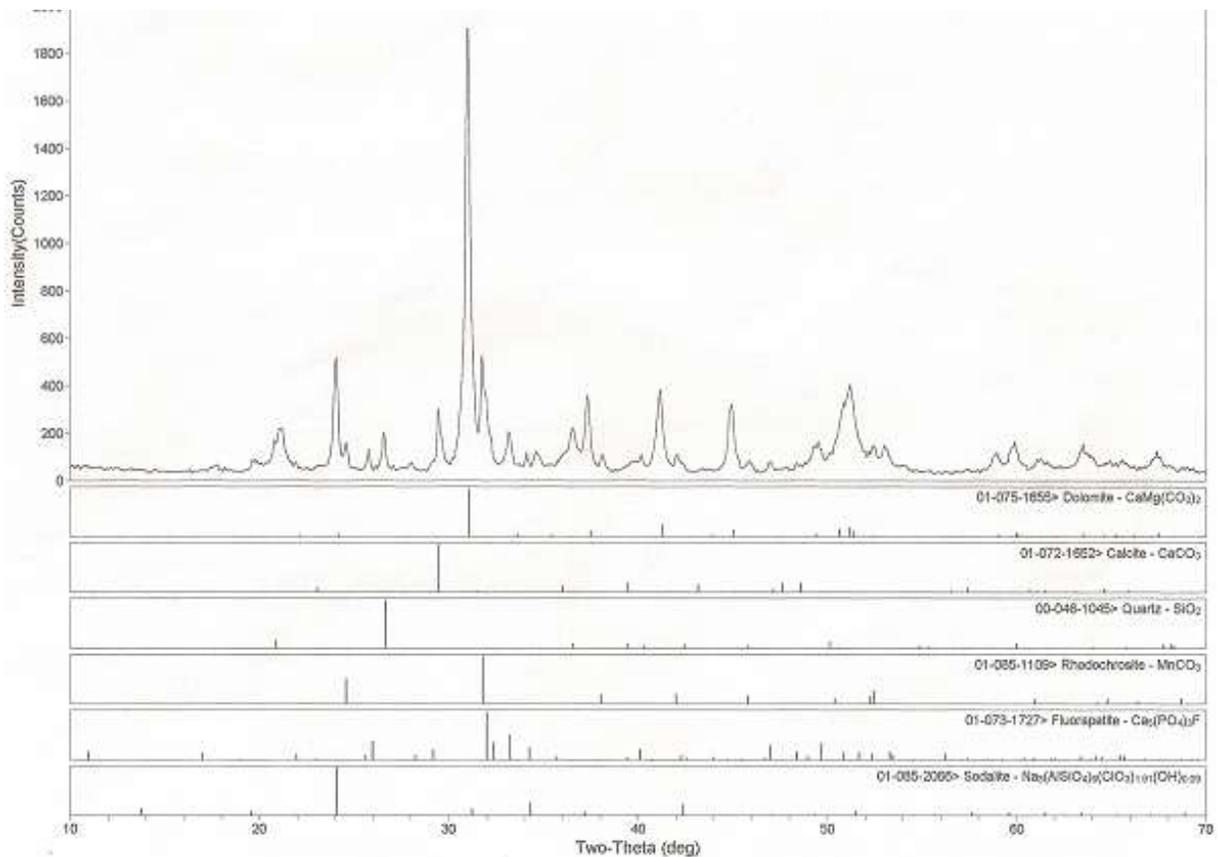


Figure 11: XRD results from the light side of the shaking table; 68.4% Dolomite, traces of Rhodochrosite, quartz and other materials.

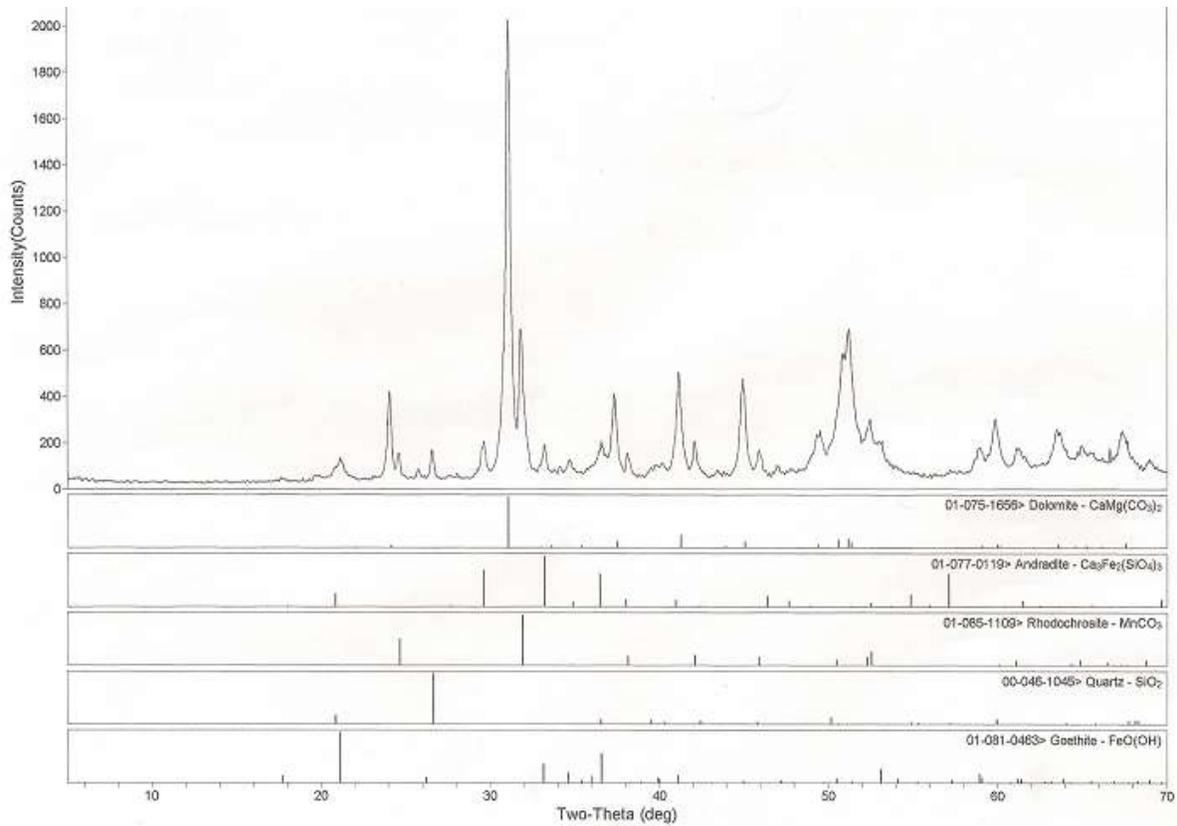


Figure 12: XRD results from the heavy side of the shaking table; 89.7% Dolomite, traces of Rhodochrosite and other materials.

Comparing Figures 11 and 12, both had a large amount of Dolomite and not much of anything else, which is baffling. Because of this, the test was rendered inconclusive.

4.4 Froth Flotation

Froth flotation is a process through which differing minerals are separated using differences in surface chemistry. Minerals are typically either hydrophilic or hydrophobic, based on control of such parameters as slurry pH, electro negativity, and the addition of collectors and depressants. Using different mechanisms to get the end result, the goal is to create a condition in which one or more minerals exhibit properties different from the bulk slurry.

In a typical flotation cell, the valuable minerals are made to be hydrophobic so that the minerals repel water and bond to air bubbles that rise through the slurry. This process results in the minerals being entrapped in a layer of froth on top of the slurry (a reagent known as a frother is typically needed to stabilize this froth bed and ensure that it exists for a sufficient duration for the enriched froth to be removed). The froth is then removed as the concentrate. In differential flotation, the desired minerals are treated to become hydrophilic and are repelled by the air bubbles. The minerals are therefore removed in the slurry in what would be the tail stream in a normal circuit, while the froth contains mostly gangue material.

There were two characteristics to consider while performing this experiment: hydrophobicity, and the point of zero charge. Because the contact angle of the rhodochrosite is relatively small (see Table 2), the chances of floating this constituent without the addition of a surfactant is implausible.

Table 2: Contact Angle of Constituents

Constituent	Contact Angle (Degrees)
Dolomite (CaMg(CO₃)₂)	6.6
Rhodochrosite (MnCO₃)	33-51
Quartz (SiO₂)	0

The conditions at which the surface charge becomes zero are of particular importance. The activity of the potential determining ions at which the surface charge is zero is called the point of zero charge (PZC) of the mineral. When the H⁺ and OH⁻ ions are potential determining, the PZC is expressed in terms of pH (7). However, because the point of zero charges on the different constituents (see Table 3) are relatively far apart, electrostatic flotation was used.

Table 3: Point of Zero Charge of Constituents

Constituent	Point of Zero Charge (PZC)
Dolomite (CaMg(CO₃)₂)	8
Rhodochrosite (MnCO₃)	5.5
Quartz (SiO₂)	2
Shale	1.0-2.0

The liquid medium used in both experiments was water, and the collector used in both experiments was dodecylamine. The frother used in the first experiment was pine oil, and in the second set was Fantastic cleaner (which includes D-glucopyranose, oligomeric, and C9-C11-alkyl glycosides). The froth that was generated using the pine oil was significantly less than using the cleaner, however since Fantastic is not a normal frother, pine oil was the chosen frother for the preceding experiments. XRD was performed on both sets of experiments to see if the frother had any effect on the concentrations.

4.4.1 XRD Results

Comparing Figures 13 and 14 (XRD results using pine oil and the cleaner respectively), the pine oil frother worked better than the cleaner. By floating the Dolomite, the material left in the flotation tank had high concentrations of rhodochrosite. Running additional experiments, the maximum rhodochrosite increase from one flotation was 43.3%.

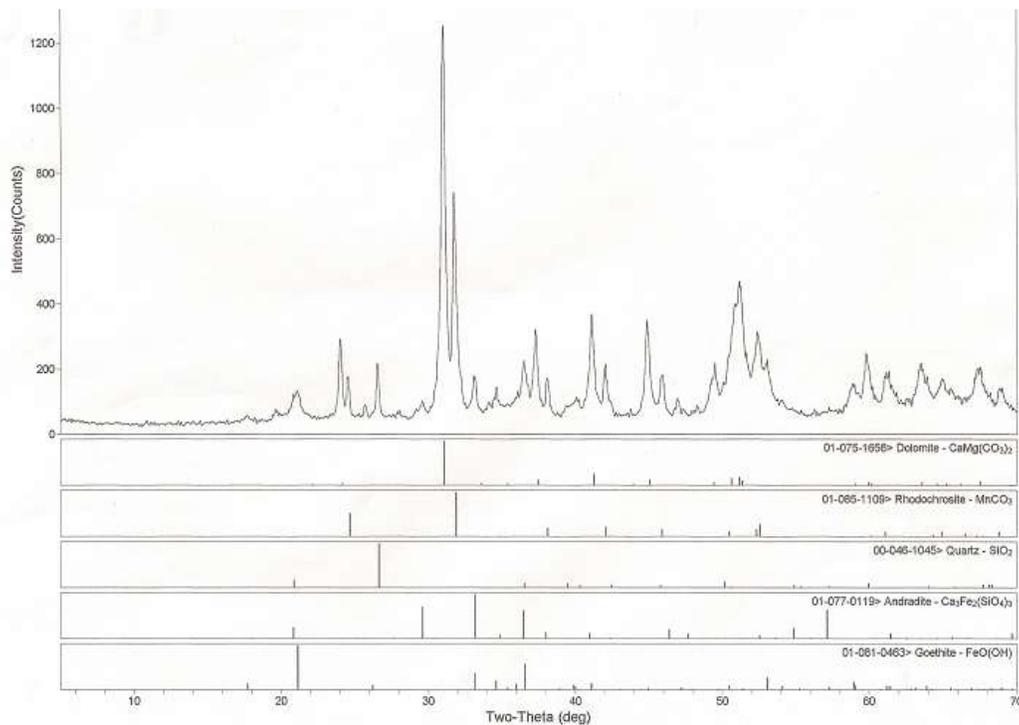


Figure 13: XRD results - froth flotation using pine oil; 89.1% Dolomite, 5.0% Rhodochrosite, traces of other materials.

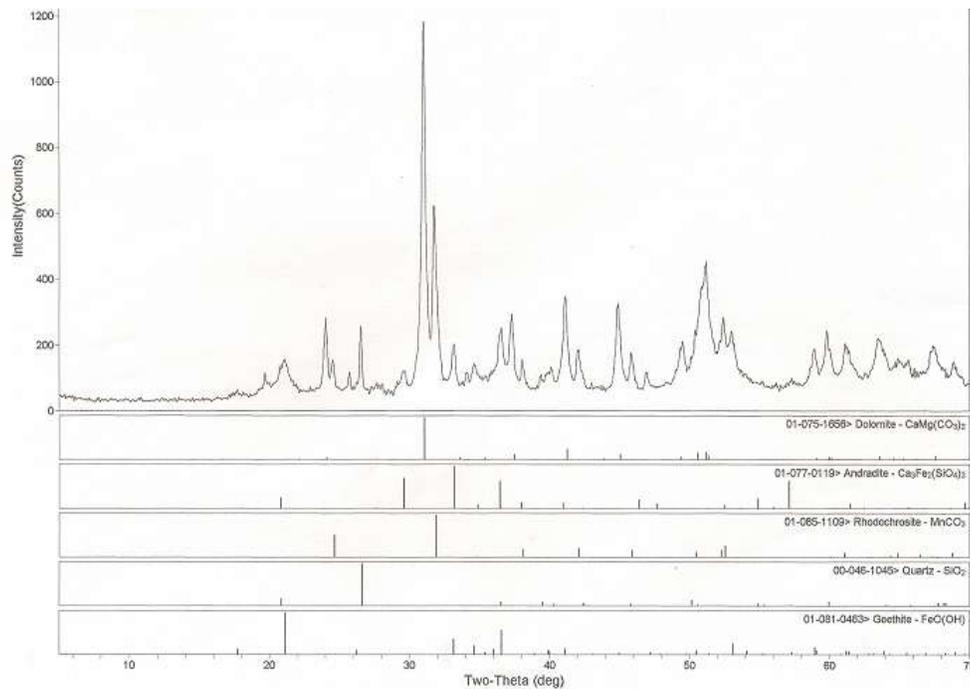


Figure 14: XRD results - froth flotation using cleaner; 72.3% Dolomite, 14.7% Rhodochrosite, and traces of other materials.

4.5 Leaching Possibilities

4.5.1 In Situ Leaching

In situ leaching is a process of recovering minerals through boreholes drilled into a deposit. If the ore body is impermeable by drilling, explosive may be used to crack into the deposit. A leaching solution is pumped into the deposit where it makes contact with the ore, creating a concentrated solution that is then pumped back to the surface to be processed; see Figure 15 for an illustration. Like all methods, there are advantages and disadvantages with in situ leaching:

Advantages:

- Possibility to mine inaccessible sites
- Shorter mine development time

- No excavating costs
- Lower mining and infrastructure costs
- Reduces visual impact of mining operations
- Personnel stays isolated from broken ore and other radiation hazards

Disadvantages:

- Permeability problems
 - Must be cracked by explosions is ore is impermeable
 - Precipitation of secondary minerals might cause problems
 - Leaching liquid may stream downwards without percolating the ore body entirely
- Risk of contamination of ground water because of poor solution control

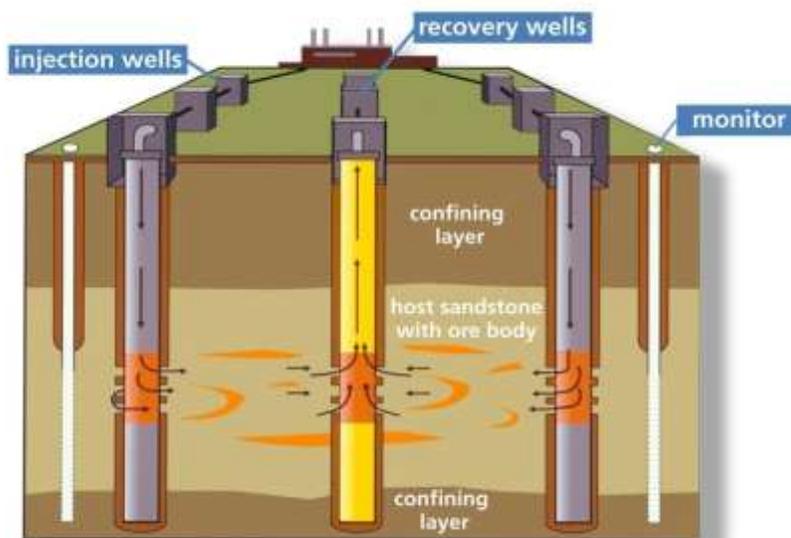


Figure 15: In situ leaching schematic according to the Silicon Investor.

4.5.2 Heap Leaching

Heap leaching is another process to extract metals from an ore body. The mined ore is crushed and heaped on an impermeable pad where the ore is irrigated with a leach solution to dissolve the valuable metals. The solution percolates through the heap and leaches out the desired metal, and is then collected. See Figure 16 for a diagram of heap leaching. Again, there are advantages and disadvantages to this leaching process:

Advantages:

- At low rates, the leachant will primarily flow through the finer particles
- At high rates, the leachant will primarily flow through courser particles

Disadvantages:

- This process can take a long time to completely extract the valuable materials

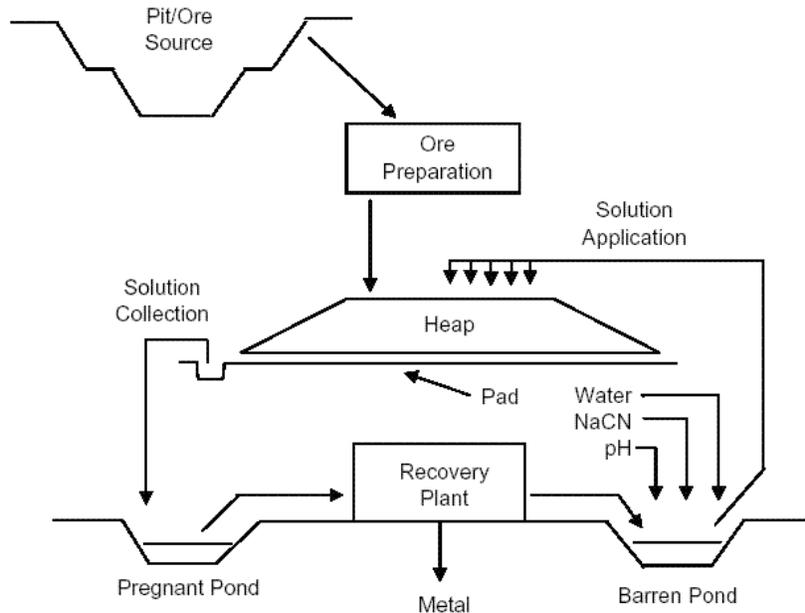


Figure 16: Heap leaching schematic according to e-gold prospecting.

4.5.3 Phase Separation (Tank/Vat Leaching)

Vat leaching is a hydrometallurgical process where the ore (after size reduction and classification) and a leaching solution are placed into a large vat (see Figure 17). Agitators within the vats improve the contact between the solids and the leaching solution. Some of the advantages and disadvantages of vat leaching are:

Advantages:

- Good process control and contact between leaching reagent and material which results in faster leaching kinetics and improved recoveries
- Rapid recovery of desired metal

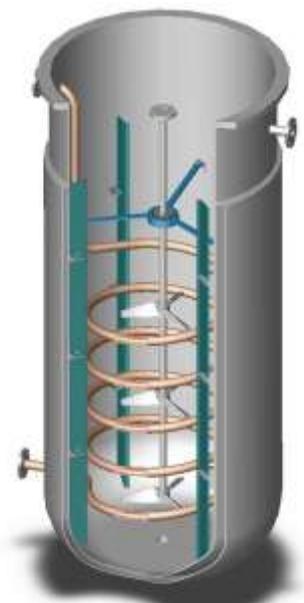


Figure 17: Vat leaching schematic.

- Relatively high extraction

Disadvantages:

- Higher capital and operating costs than heap leaching

4.6 Solid-Liquid Separation

Hydrometallurgical processing typically creates abundant colloidal solids during the leach step. Proper liquid-solid separation enables recovering the maximum amount of pregnant liquor while minimizing its dilution. Thus, multistage countercurrent sedimentation, countercurrent washing filtration on a single filter, or two- or three-stage filtrations with single washes per stage are practiced. The mineral or metal is commonly precipitated from solution and washed to maximize purity. Thus, both continuous vacuum filters and pressure filters are involved. Many factors external to the liquid-solid separation equipment itself influence its performance and productivity. The most common of these follow:

1. Particle size and shape
2. Weight and volume percentage of solids
3. Fluid viscosity and temperature
4. pH and chemical composition of the feed
5. Variation and range in feed quality (items 1-4)
6. Specific gravity of solids and liquid
7. Quality requirements of discharge streams from liquid-solid separation steps, particularly as they influence results upstream and downstream (5).

5. Broader Impact

Because of manganese's utility and value, a profitable mine in central South Dakota has enormous beneficial impact. Manganese is considered to be critical to national defense (12) and for such a mineral to be 100% imported is a liability. A substantial source for manganese in the United States also would decrease the price for consumers by reducing shipping expenses

and eliminating tariffs. This decrease in expenses ultimately equals more affordable steels. This domino effect of lower expenses has the potential to make the US more competitive on a global scale for steel production.

The possibility of mining the Missouri River manganese nodules raises several concerns and issues. This central South Dakota deposit is unquestionably the largest manganese ore deposit in North America, but as previously stated, the low metal content makes mining the deposit profitably difficult (11).

The harsh winter conditions raise a concern about mine development in this area. On average, almost fifty inches of snow fall annually in Chamberlain, South Dakota (10). Snow and extreme winter weather notoriously slow production of mines and are known for halting operations completely. Even though a harsh winter climate can stress production, it typically is not the deciding point on whether development occurs. For instance, the arctic gold mines of Russia and the northern diamond mines of Canada battle climate condition far more strenuous than those which would be experienced mining the Missouri nodules. These mines do report costly mining operations, and their isolated location makes acquiring supplies a higher cost.

A beneficial characteristic that supports a mine in this area is the fact that much of the ore is near the surface, making extraction much more inexpensive in comparison to an underground operation. This outcropping and large flat ore deposits suggest that strip mining would be the most cost effective method of extraction (12). Strip mining is a form of surface mining that consists of removing an upper layer of rock to expose a typically shallow ore deposit and in this operation, here the 15-17% manganese nodules.

6. Conclusion

After a great deal of work, a few important advances in the manganese recovery of the Missouri River nodules have been made. Through lab scale experiments, a construction of manganese ore suitable for sale was completed through one of the processing methods. During the many processing techniques tested, the use of floatation was the most productive. The

research team investigated this deposit and determined that an operating manganese mine in the United State would have significant benefits in decreasing concerns of acquiring this strategic metal. With research and physical observation, characteristics vital to mine construction have now been documented and with the new gathered knowledge concerning the ore, a strip mining surface mine would be an efficient method of extraction of the Missouri River nodules located near the Chamberlain area.

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