ENHANCED REMOVAL OF DOLOMITE PEBBLE CONCENTRATE BY CO$_2$ GENERATION

FINAL REPORT

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MICHIGAN TECHNOLOGICAL UNIVERSITY

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August 2009

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ENHANCED REMOVAL OF DOLOMITE PEBBLE CONCENTRATE
BY CO$_2$ GENERATION

FINAL REPORT

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August 2009

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PERSPECTIVE

Patrick Zhang, Research Director - Beneficiation & Mining

With the depletion of the higher-grade, easy-to-process Bone Valley deposits, the Central Florida phosphate industry has moved into the lower-grade, more contaminated ore bodies from the Southern Extension. The phosphate deposits in the Southern Extension may be divided into two zones: an upper zone and a lower zone. The upper zone is readily amenable to the current processing technology, but the lower zone is highly contaminated by dolomite and requires a new method. Dolomite is generally concentrated in the pebble fraction, typically within the size range of 1 to 20 mm. Geological and mineralogical statistics show that up to 50% of the phosphate resource would be wasted if the lower zone is bypassed in mining, and that about 13% of the phosphate resource would be wasted if the lower zone is mined but the dolomitic pebbles are discarded.

Perhaps the most promising process for Florida dolomitic phosphate pebbles is the CLDRI process developed under FIPR funding. In this process, dolomitic pebbles are ground to suitable particle sizes (normally to -100 mesh) for liberating dolomite and other impurities from phosphate. The ground slurry is subject to dolomite flotation followed by either silica or phosphate flotation. A recently completed pilot-scale testing of the CLDRI process on dolomitic pebbles from IMC and CF Industries has demonstrated both the technical and economical feasibility of the CLDRI process. However, capital cost, in tens of millions of dollars for a new flotation plant, and energy cost and materials handling problems associated with fine grinding are believed to be major hurdles to commercialization of the CLDRI process.

The method of separation initially proposed in this investigation centers on the fact that the high-dolomite particles will generate CO_2 when exposed to a slightly acidic solution. This generation of CO_2 will reduce the apparent density of dolomite particles, rendering better separation using gravity separation equipment, in this case, a jig. However, success was achieved by abandoning the CO_2 generation idea and focusing instead on improving jigging using techniques based on gravity separation principles.

The Michigan Tech researchers have demonstrated that a product of less than 1% MgO could be achieved at P_2O_5 recovery of up to 67% from high-dolomite pebbles without grinding. Considering that no grinding is required for this process and that jigging is one of the least expensive minerals separation methods, these results are indeed quite encouraging and should warrant an evaluation of a continuous process using this technique.

ABSTRACT

The objective of this project is to take advantage of the generation of CO_2 gas by dolomite in contact with acid to enhance physical separations based on density, to reject as much dolomite as possible without sacrificing phosphate recovery. The first phase of the project was to obtain samples of high-dolomite phosphate pebble, provided by Mosaic Inc., and to characterize this material to determine the quantities and distribution of magnesium-bearing minerals. It was found that the dolomite was preferentially concentrated in the coarse fraction, and that the dolomite and phosphate minerals were well-liberated from each other even at the coarse sizes. The -6 mesh material had a sufficiently low dolomite content that it was very close to being an acceptable product even without further dolomite separation.

The second phase of the project was to construct an acid-resistant jig, and use it to carry out density separation of dolomite from the phosphate minerals. Studies were first conducted to determine the extent to which jigging could upgrade the phosphate in the absence of acid. It was determined that the jig could achieve significant levels of dolomite removal using only water as the separating media, due to the small difference in density between the apatite particles and the dolomite particles. The phosphate minerals were found to be broadly classifiable into a lower-density and a higher-density form, and the higher-density phosphate was found to be amenable to concentration by jigging.

Subsequent experiments were carried out to determine the extent to which the addition of acid and the generation of carbon dioxide gas could improve jig performance, and whether the performance could be enhanced further by the use of surfactants to help bubbles to adhere preferentially to the dolomite surfaces.

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INTRODUCTION

Phosphate rock is a fundamental commodity used in the production of certain types of fertilizers. With the worldwide demand for fertilizers continuously rising, high grade phosphate reserves are becoming depleted. However, there is an abundance of low grade phosphate ore available that contains dolomite impurities. The dolomite $(CaMg(CO_3)_2)$ must be removed from the phosphate ore or it will cause problems during the fertilizer production process. Due to the close mineralogical similarities between dolomite and apatite (phosphate mineral, $Ca_5(PO_4)_3(F,OH,Cl)$), an efficient and cost effective method for dolomite removal has not yet been developed. The overarching objective of this project is to investigate the feasibility of jigging as a method for separating dolomite from apatite in high-dolomite phosphate ores.

The majority of the phosphate rock mined goes into producing phosphoric acid. Phosphoric acid is produced by reacting a phosphate mineral (apatite) with sulfuric acid and water as shown below in reaction (1).

$$Ca_3(PO_4)_2(s) + 3H_2SO_4(l) + 6H_2O(l) \rightarrow 2H_3PO_2(s) + 3CaSO_4 \cdot 2H_2O(s) \qquad (1)$$

$$\underbrace{Ca_3(PO_4)_2(s)}_{\text{Phosphate}} \qquad\qquad \underbrace{2H_3PO_2(s)}_{\text{Phosphoric Acid}}$$
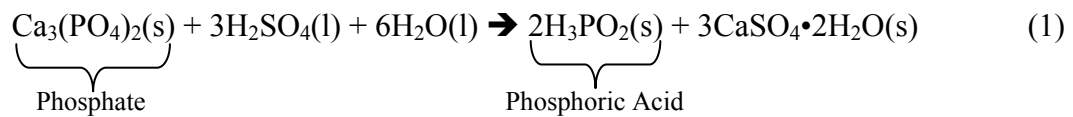
In the case of the high-dolomite phosphate ore, the dolomite $(CaMg(CO_3)_2)$ must be removed to minimize MgO content. Phosphate rock containing large amounts of dolomite impurities will result in increased sulfuric acid consumption and slower filtration rates during the phosphoric acid production process. In general, useful phosphate rock must contain less than 1% MgO.

THEORETICAL DISCUSSION

Gravity separation is any method in which minerals of different specific gravity are separated by their relative movement in response to gravity and one or more other forces. There are many different types of gravity separation techniques available, which include: jigging, shaking tables, spirals, and heavy media separators. Our research focuses on using jigging as a process for separating dolomite from apatite. Jigging is attractive for this application for many reasons: (1) Jigs can work with coarse particles, so grinding costs are eliminated; (2) Jigging is relatively inexpensive compared to heavy media separation and flotation; (3) Jigs can be highly selective if operated correctly.

JIGS

Jigging is a process in which light particles are separated from heavy particles by the continuous expansion and compaction of a particle bed. Figure 1 shows a diagram of a Harz jig. The particle bed sits on top of the screen while a plunger moves up and down resulting in cycles of pulsation and suction strokes. Pulsation and suction strokes cause the particle bed to expand and contract, which results in the stratification of the particle bed. A "hutch water inlet" allows a constant upward flow of water through the jig, ensuring fluidization and expansion of the particle bed.
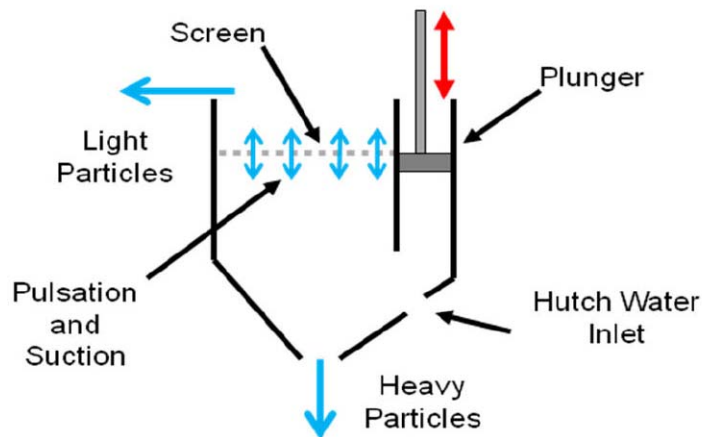
Figure 1. Diagram of Jig.
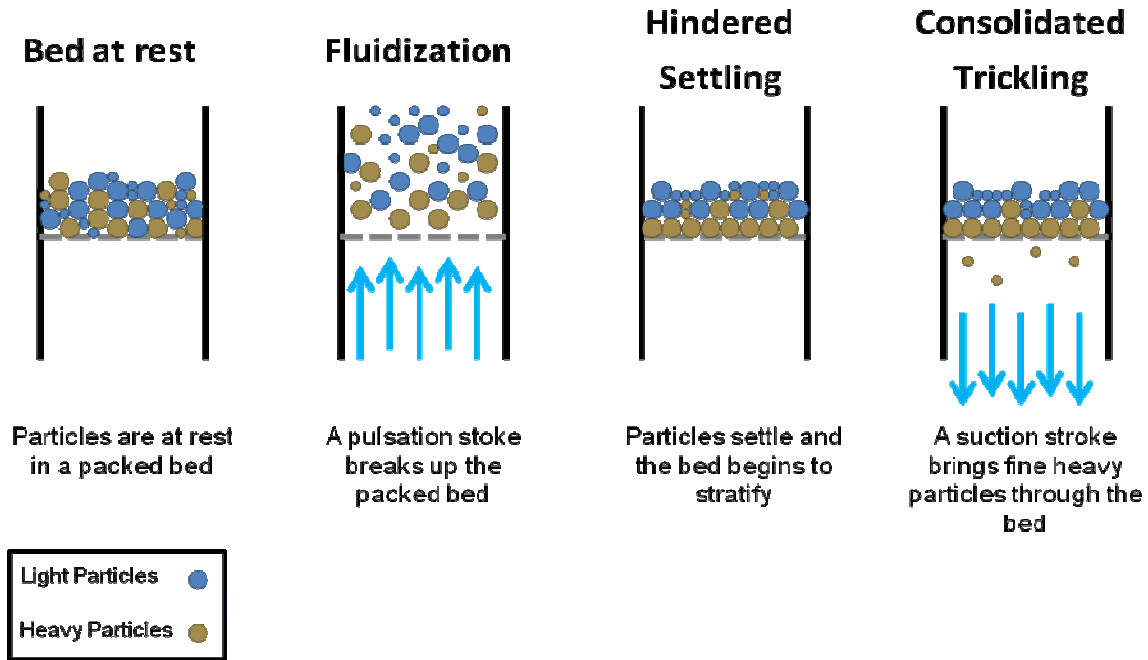
Figure 2. Methods of Particle Stratification through the Jigging Process. (Adapted from Gupta and Yan 2006.)

JIGGING PROCESS

Figure 2 shows an in-depth look at the mechanisms of separation that occur during the jigging process. The first mechanism of separation is *initial differential acceleration,* which occurs at the very beginning of the pulsation stroke. Initial differential acceleration separates purely on density differences. The second mechanism of separation, *hindered settling,* occurs during the pulsation stroke and leading into the suction stroke. Hindered settling separates particles based on differences in settling rates. Since particle settling rates are mainly a function of particle density and particle diameter (other properties such as particle shape and fluid properties also affect settling rates), hindered settling depends on both particle density and diameter.

The final mechanism of separation is *consolidation trickling*, in which the suction stroke pulls smaller heavy particles through larger heavy particles on top of the screen. The typical jigging process can be described describe as a sine wave as shown in Figure 3 (Falconer 2003). Positive fluid flow velocity corresponds to the pulsation stroke while a negative fluid flow velocity corresponds to the suction stroke. At *Point A* the pulsation stoke begins to break apart the particle bed and initial differential acceleration occurs.

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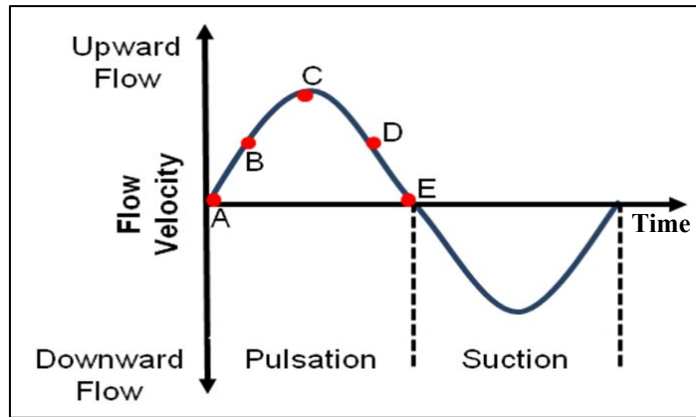
Figure 3. Fluid Flow Model for Jigging Process. (Adapted from Wills 1985.)

Hindered settling in the upward flow takes over around *Point B*. The fluid velocity is at its greatest at *Point C* and we must be careful not to push fine heavy particle to the top of the jig bed and out the overflow. At *Point D* hindered settling continues as the fluid velocity begins to slow down. The suction stroke takes over at *Point E* and consolidation trickling pulls the fine heavy particles through the screen.

HUTCH WATER ADDITION

In some cases, the particle bed will compact tightly during the suction stroke obstructing the consolidation trickling phase. The addition of a constant flow through the jig bed (hutch water flow) helps to alleviate this problem. Figure 4 shows the results from the addition of hutch water. The addition of hutch water simply shifts the flow velocity curve upwards, which consequently reduces both the magnitude and duration of the suction stroke.
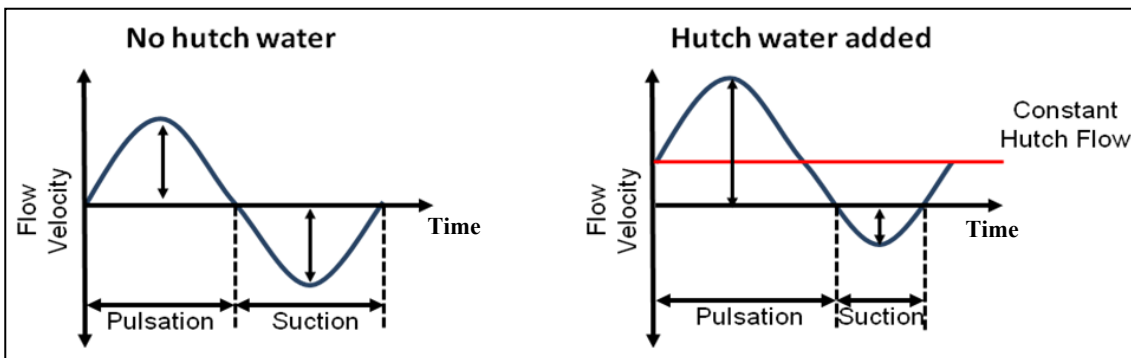
Figure 4. Effects of Hutch Water Addition. (Adapted from Wills 1985.)

EFFICIENCY OF JIGS

Since jigging is a gravity separation process, the efficiency of the jigging process depends on density differences between the separated minerals. As a rule of thumb, the concentration criterion shown in Equation (2) can be used to describe the difficulty of the separation. A concentration criterion less than 1.25 means that the separation is not generally economically feasible with the types of equipment currently available (Wills 1985). When using the literature values for Apatite (S.G.≈3.2) and Dolomite (S.G.≈2.85), with water as the working fluid (S.G.≈1), the concentration criterion equals 1.19. This means that we need to look into ways of increasing the concentration criterion of the separation.

$$Concentration \quad Criterion = \frac{D_h - D_f}{D_l - D_f} \qquad (2)$$

One way to increase the efficiency of the jigging process would be to increase the apparent density difference between the minerals. It was decided to look at the fact that the dolomite pebbles produce CO_2 bubbles when in the presence of an acid solution as shown in reaction (3).

$$MgCa(CO_3)_2(s) + 2H_2SO_4(aq) \rightarrow (Ca,Mg)SO_4(aq) + 2H_2O(l) + 2CO_2(g) \qquad (3)$$
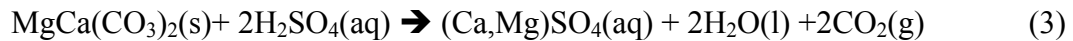
Previous research done by El-Midany (2004) has shown it is possible to float pebble-sized dolomite from apatite through a reactive flotation process with certain surfactants. El-Midany indicated that the most promising surfactants were some anionic surfactants and polyvinyl alcohol (PVA). In the present study, the investigators were not looking to float the dolomite, but simply lower the apparent density of the dolomite enough to make gravity separation economically feasible. They also wanted to avoid using expensive surfactants, if possible. Figure 5 shows their hypothesis of how the CO_2 bubbles would decrease the apparent density of the dolomite. It should also be noted that the dolomite pebbles are somewhat porous. It is hypothesized that CO_2 bubbles produced by the reaction of acid and dolomite will push water out of the pores and further decrease the apparent density of the dolomite pebbles.
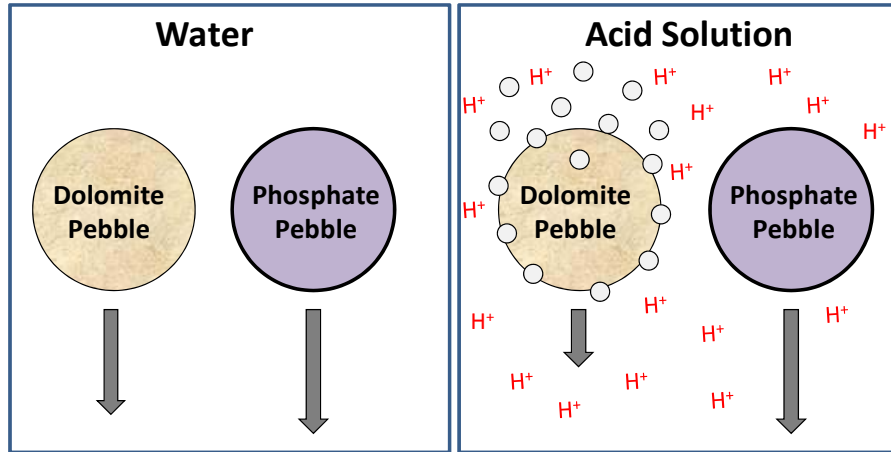
Figure 5. Decreasing the Apparent Density of Dolomite.

A second way to increase the concentration criterion may lie in the working fluid. Considering the concentration criterion equation once more, it can be seen that if the density of the fluid was increased, the concentration criterion would also increase. In theory, as the density of the fluid (D_f) approaches the density of the light mineral (D_l), the concentration criterion approaches infinity. If the density of the fluid was greater than the density of the light mineral, there would essentially be heavy media separation. One problem with increasing the density of the working fluid is that dense fluids are typically made up of fine, heavy particles suspended in a fluid such as water. Increasing the density of the fluid enough to make heavy media separation possible significantly increases the viscosity of the fluid, which consequently hinders particle movement. However, it is practical to increase the density enough to improve the concentration criterion without greatly increasing the viscosity.

PREPARATION AND CLASSIFICATION OF HIGH-DOLOMITE PHOSPHATE ORE

PREPARING REPRESENTATIVE SAMPLES

High-dolomite phosphate ore samples were received from Mosaic in two 55-gallon barrels. Each 55-gallon barrel was separated into representative samples that could be tested to determine mineral compositions. It was decided to split each 55-gallon drum separately and compare the results. Figure 6 shows the process used to split each of the 55-gallon barrels. The barrel was first split into halves using a large riffle splitter. One half was split into halves again using a large riffle splitter. One quarter of each barrel was then split into three different size fractions by screening. The desired size fractions for the analysis were +3 mesh, -3/+6 mesh, and -6 mesh. Previous work has shown that large amounts of dolomite are present in the coarse-size fractions while smaller-size fractions contain considerably less dolomite. Each size fraction was then split into twelfths using a rotary splitter. One-twelfth was taken from each size fraction and crushed more finely using a short-head crusher followed by a roll crusher. Next, the samples were split into twelfths again using a rotary splitter. Lastly, the one-twelfth (approximately 100g each) of the finely crushed samples were pulverized into a fine powder using a puck mill.
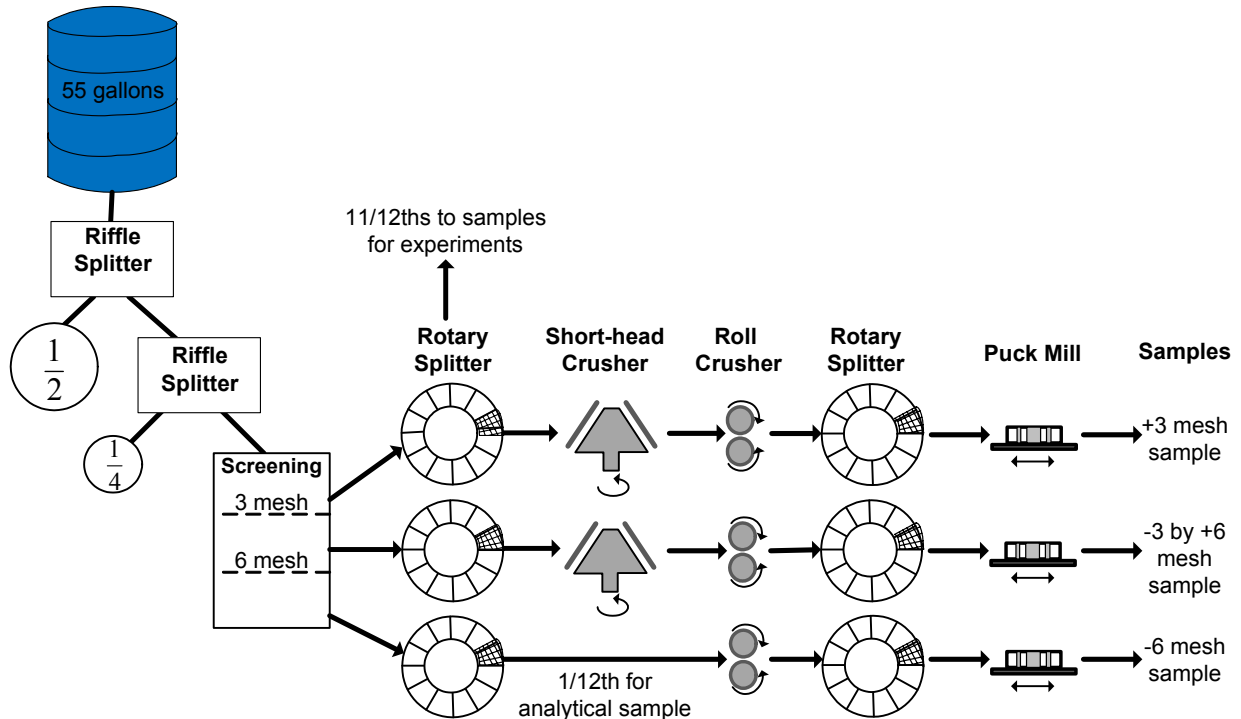
Figure 6. Method for Splitting Each 55-Gallon Barrel into Representative Samples.

X-ray diffraction (XRD) was used to determine the minerals present in each of the three size fractions (+3 mesh, -3/+6 mesh, and -6 mesh). The x-ray diffraction results

also show the relative amounts of each mineral present in the ore. Figure 7 shows the XRD results for all three size fractions. The most important result that can be seen from this analysis is that the dolomite peak (1) gets smaller as the size fractions decrease from +3 mesh to -3/+6 mesh to -6 mesh. This means there is the potential to remove a large amount of magnesium using a simple screening procedure.

ATOMIC ABSORPTION SPECTROMETRY

Atomic absorption (AA) spectrometry was used to determine the amount of Mg and Ca present in each of the size fractions. The samples were prepared by dissolving 0.5g of ore in 25mL of hydrochloric acid, then diluting to specifications. The AA used was a Varian fast sequential atomic absorption spectrometer, model number AA240FS. Mg results were converted to MgO by multiplying by 1.658 (ratio of M.W. of MgO divided by M.W. of Mg). Table 1 shows the results from the atomic absorption spectrometry. The MgO content decreases as the ore is screened to finer size fractions.
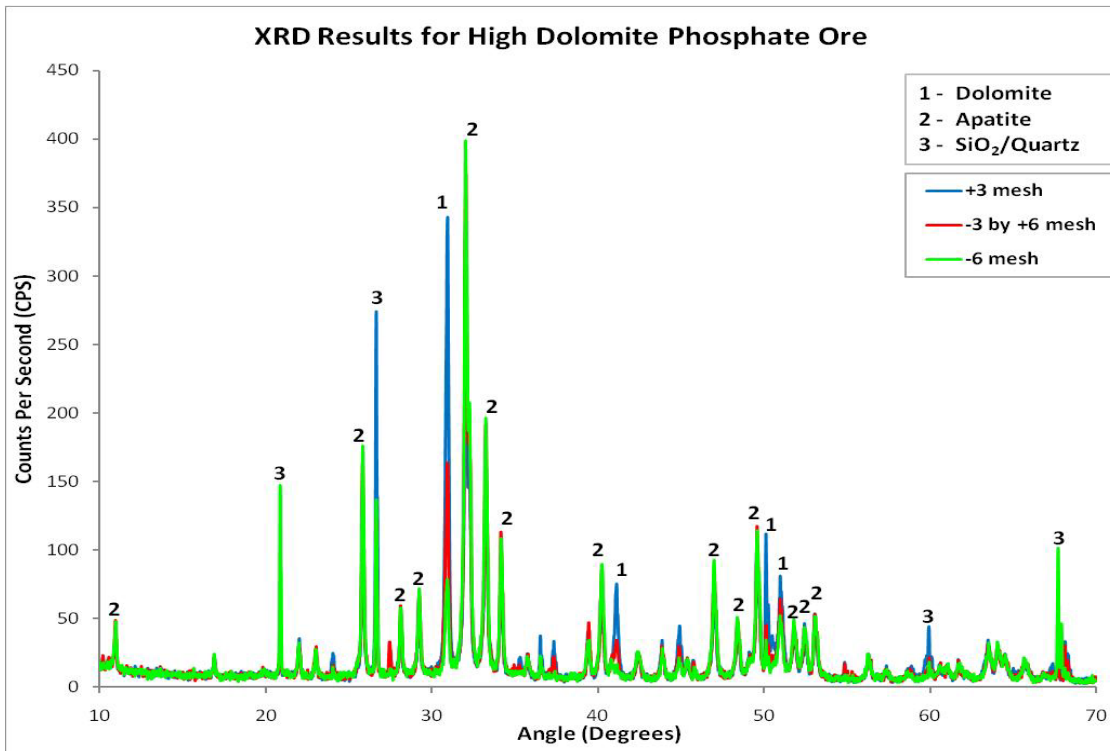
Figure 7. XRD Analysis of Mosaic Phosphate Ore.

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Table 1. Atomic Absorption Spectrometry Results for High-Dolomite Phosphate Ore.

		-6 Mesh (%)	-3 by +6 Mesh (%)	+3 Mesh (%)
Barrel 1	MgO	1.53	3.28	5.29
	Ca	29.90	29.44	27.64
Barrel 2	MgO	1.79	3.68	6.27
	Ca	29.38	32.75	30.48

SIZING OF HIGH-DOLOMITE PHOSPHATE ORE

As mentioned in the previous sections, it was decided to focus on three specific size fractions for this study. The amount of each size fraction in the sample will be an important factor in developing a method for purifying high-dolomite phosphate ore. During the splitting process shown in Figure 6, each size fraction was weighed before going through the first rotary splitter. Figure 8 shows the weight percents for each size fraction in Barrel 1 and Barrel 2. Since the amount of MgO varies with the size fraction, it may be possible to reject a large amount of magnesium through a sizing process. More importantly, optimizing jigging parameters depends greatly on the size of particles being processed. The results show that the -6 mesh size fraction makes up about 50 weight % of the high-dolomite phosphate ore, with the remaining weight split between the two coarser size fractions.
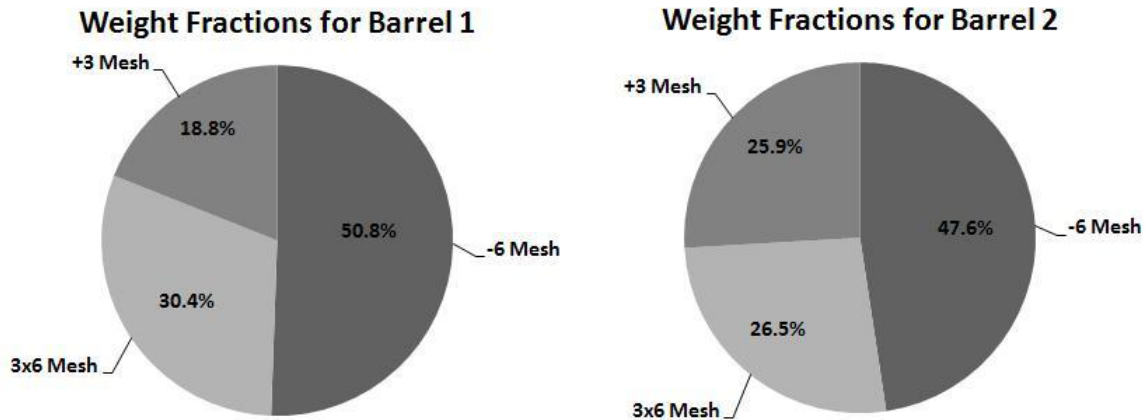
Figure 8. Total Weight Percents for Barrel 1 and Barrel 2.

LIBERATION STUDIES

Removing dolomite from the phosphate sample at coarse (-3/+6 mesh) size fractions without major phosphate losses requires that the dolomite be liberated from the apatite. Mg impurities have been shown to be present in three different forms in francolite (high-dolomite phosphate ore): (1) Ionic substitution in the crystal lattice

apatite; (2) Dolomite in apatite pebbles; (3) Discrete dolomite pebbles (Moudgil and others 1991).

To test for liberation, 10 pebbles were randomly selected from the coarsest size fractions (+3 mesh and -3/+6 mesh). Each pebble was analyzed for Mg content using atomic absorption spectrometry. Pebbles that contain a high percentage of Mg (approximately 13%) can be considered almost pure dolomite. Conversely, pebbles that contain very little Mg will also indicate liberation of dolomite from apatite. The results are shown in Figure 9 as a histogram. The histogram shows that the majority of the pebbles fell into low (0-1% Mg) or high (11-12% Mg and 12-13% Mg) percent Mg categories. This indicates that the dolomite is predominantly liberated at even the coarsest size fractions.

It should be noted that the pebbles falling into the 0-1% Mg category contained an average of 0.60% MgO, which is consistent with literature values (Lawver and others 1982, Moudgil and others 1991, McClellan 1980). This would indicate that there is some minimum MgO value that can be reached.
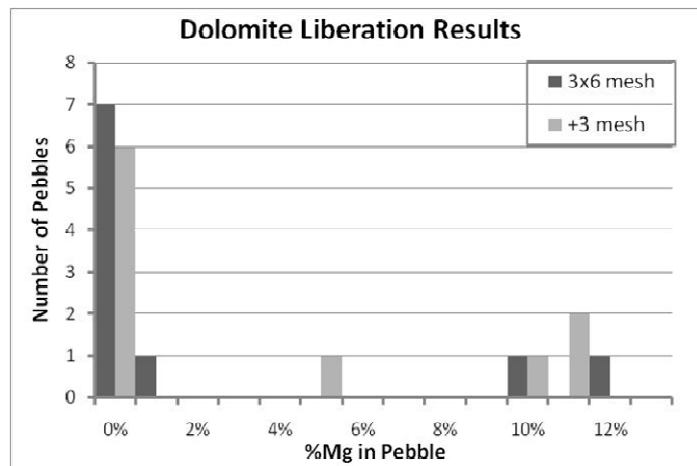
Figure 9. Dolomite Liberation Histogram.

DENSITY STUDIES

Determining densities of the pebbles making up the high-dolomite phosphate ore gives a good indication of how well jigging will work. Previously, the concentration criterion for this separation was calculated using literature density values for apatite and dolomite. The pebbles in the high-dolomite phosphate ore are most likely not pure dolomite and pure apatite in their crystal forms. Since the high-dolomite phosphate ore is made out of different color pebbles, the pebbles could be separated by hand. Each color category could then be examined using XRD to determine mineral composition. Figure 10 shows the three different color categories into which the ore was separated.

**Figure 10. The High-Dolomite Phosphate Ore Was Hand-Separated into Three
        Main Categories by Color and Texture.**

The dark black pebbles, light gray smooth pebbles, and light yellow porous pebbles were analyzed using XRD. The results are shown below in Figure 11. The graph shows that the light yellow porous pebbles are indeed dolomite. Another interesting thing to note is that the light yellow porous pebbles contain the most silica. Finally, the dark black pebbles and light gray pebbles are both apatite. This brings up some interesting questions: Why are the black and light gray pebbles different in color if they are both apatite, and do they exhibit different properties such as density?
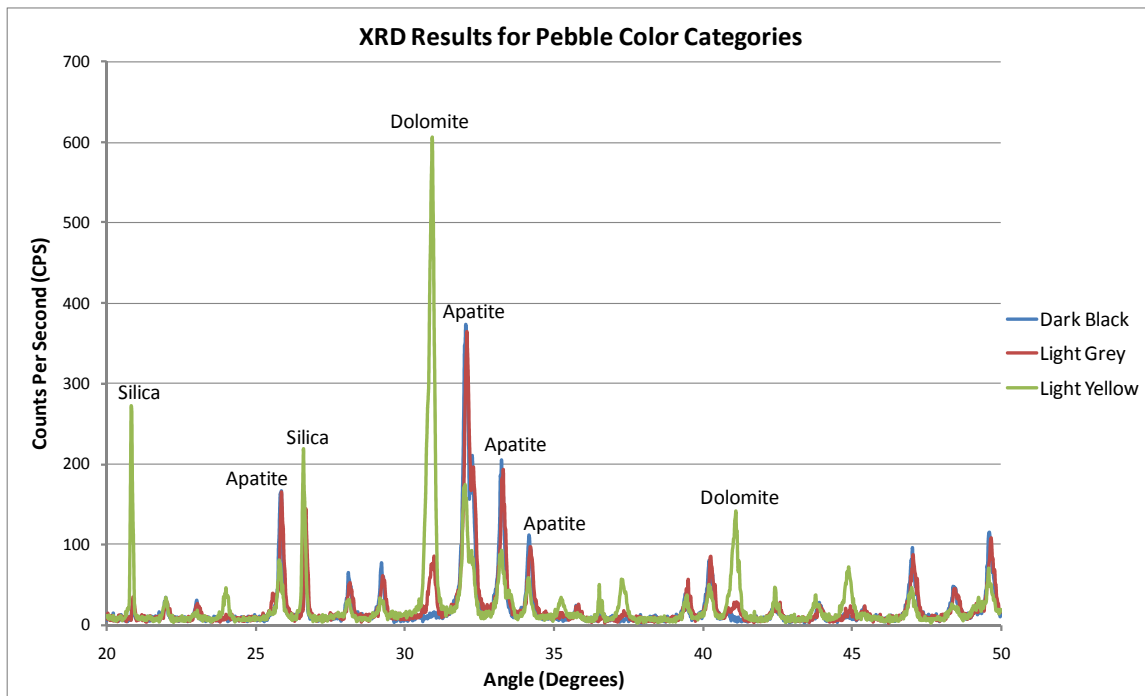
Note: The dark black and light gray pebbles are apatite. The light yellow porous pebbles are dolomite.

Figure 11. XRD Results for Pebble Color Categories.

The density of each pebble type was measured using two different methods. First, the densities were calculated using a 25mL pycnometer. Ten grams of each pebble type

were put into a 25mL pycnometer and filled with distilled water. The pycnometer was rotated gently for about two minutes to make sure no air bubbles were trapped between the pebbles. The results are shown below in Table 2.

Table 2. Density Measurements Using 25mL Pycnometer.

Type	Density (g/cm^3)
Dark black pebbles (apatite)	2.78
Light gray smooth particles (apatite)	2.55
Light yellow porous pebbles (dolomite)	2.51

The dark black apatite pebbles had the highest density at 2.78g/cm^3 while the light yellow dolomite pebbles had the lightest at 2.51g/cm^3. The light gray apatite pebbles showed a low density compared to the dark black apatite pebbles. This would decrease the jigging efficiency, as some of the apatite would go to the top of the jig bed with the dolomite. It is important to know why the densities are so different between the dark black and light gray apatite pebbles.

One possible explanation for the large difference in density between the dark black and light gray apatite pebbles is porosity. The light gray pebbles may be more porous than the dark black pebbles. To determine how the density of each pebble type changes when immersed in water, a device that measures density based on Archimedes' principle was used. The instrument setup is shown below in Figure 12. The density measurement is based on the fact that any object, wholly or partly immersed in a fluid, is buoyed up by a force equal to the weight of the fluid displaced by the object.
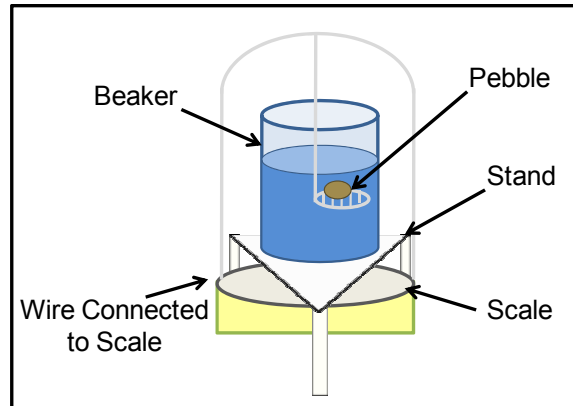
Figure 12. Archimedes' Principle Density Measuring Device.

The density of each pebble was measured over a period of four minutes by taking measurements every minute. The results can be seen below in Figure 13. The results showed that the dark black apatite pebbles were not porous, as the density measurement stayed constant at approximately 2.85g/cm^3, which is consistent with the density measurements made using the 25mL pycnometer. Density measurements for the light gray apatite pebbles showed an increasing trend over the four minutes. This indicated

that they were in fact porous and when left in water long enough, the apparent density of the light gray apatite pebbles could possibly increase to that of the dark black apatite pebbles. The light yellow dolomite pebbles showed a quick increase in density within the first two minutes but then leveled off and actually decreased slightly. This indicated that the light yellow dolomite pebbles had larger pores than the light gray apatite pebbles, as the water could replace the air more rapidly. It is important to know the density of each pebble type over time because the efficiency (concentration criterion) will change depending on the total jigging time.
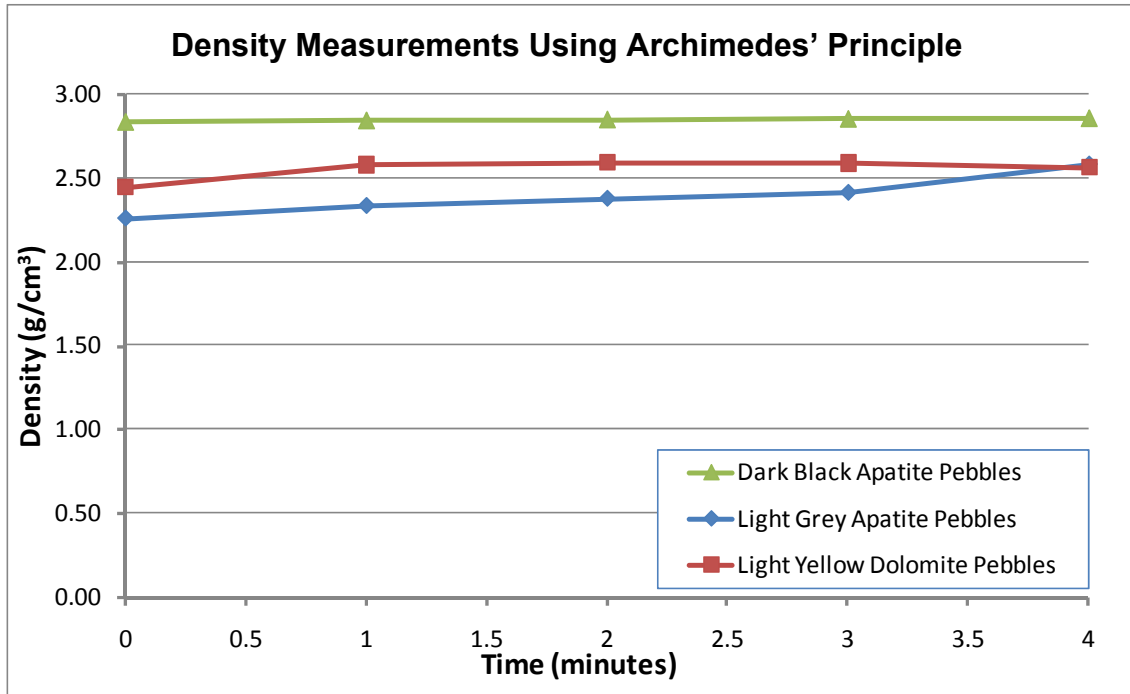
Figure 13. Density Measurement Results Using Archimedes' Principle Device.

JIGGING EXPERIMENTAL SETUP

DESIGNING AN ACID-RESISTANT JIG

Two jigs were available in the lab at the beginning of this project. Unfortunately, both jigs were constructed of metal parts that were not acid-resistant, and did not allow for easy adjustments of the jigging parameters. More importantly, the jigs were relatively small which could result in sampling issues when using a -3/+6 mesh pebble-sized feed. This meant that it was necessary to custom-build jigs for the experimental work. Figure 14 shows a diagram and photograph of the first version of the jig, which is referred to as the air pulsation jig. The main body of the jig was made of 4" PVC pipe with the pulsation arm being made of 2" PVC pipe. The screen was a 10 mesh stainless steel screen. Unions were used to connect the top piece (jig bed and screen) to the main part of the jig. This made the jig easy to take apart when testing. Unions also made it possible to modify different parts of the jig without having to rebuild the whole jig.
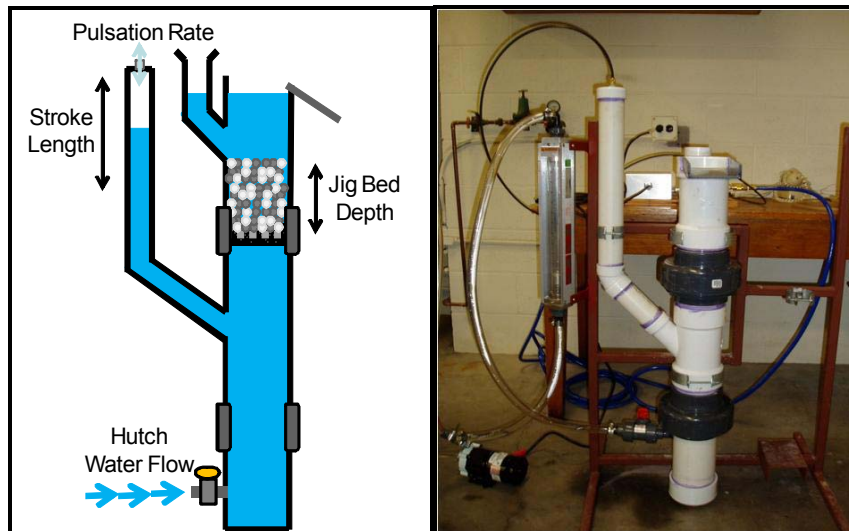
Figure 14. Air Pulsation Jig (left: air pulsation jig with important adjustable parameters; right: air pulsation jig in lab.)

The pulsation controller is shown below in Figure 15. There was an air pressure regulator that controlled the pressure of the air going into the air chamber. This allowed the jig's stroke length to be changed. A solenoid valve and controller were used to vary the pulsation rate.

Figure 15. Air Pulsation Control System.

JIG MODIFICATIONS

During initial jig testing, it became apparent that there were some problems with the air pulsation jig. The main problem was that when attempting to reach higher pulsation rates (over 60 pulse/min.) large air bubbles were pushed through the jig. Figure 16 shows the modifications made to the jig to alleviate this problem. A plunger pulsation system allowed higher pulsation rates to be reached without pushing large air bubbles through the jig. The first version of the plunger pulsation jig used a slightly smaller motor than the current version. Figure 17 shows the current plunger pulsation jig being used for testing. Also pictured are the new controller and motor capable of reaching pulsation rates greater than 500 pulse/min. The top piece of the jig was also shortened to allow for easier testing.

Large air bubbles go through the system at high pulsation rates

Plunger style jig eliminates air bubbles and allows for higher pulsation rates
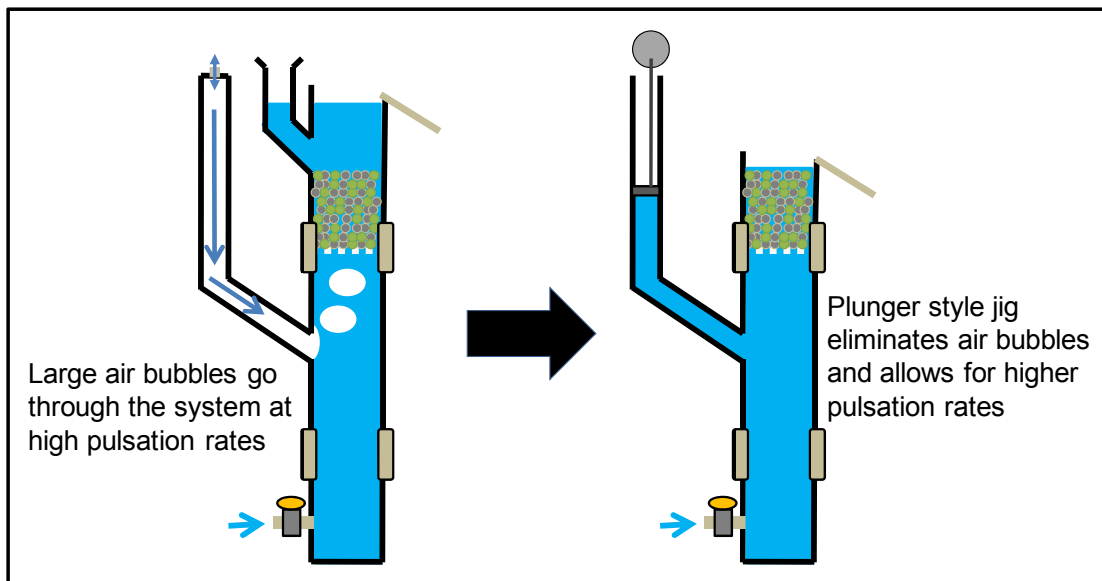
Figure 16. Modifications to Air Pulsation Jig.
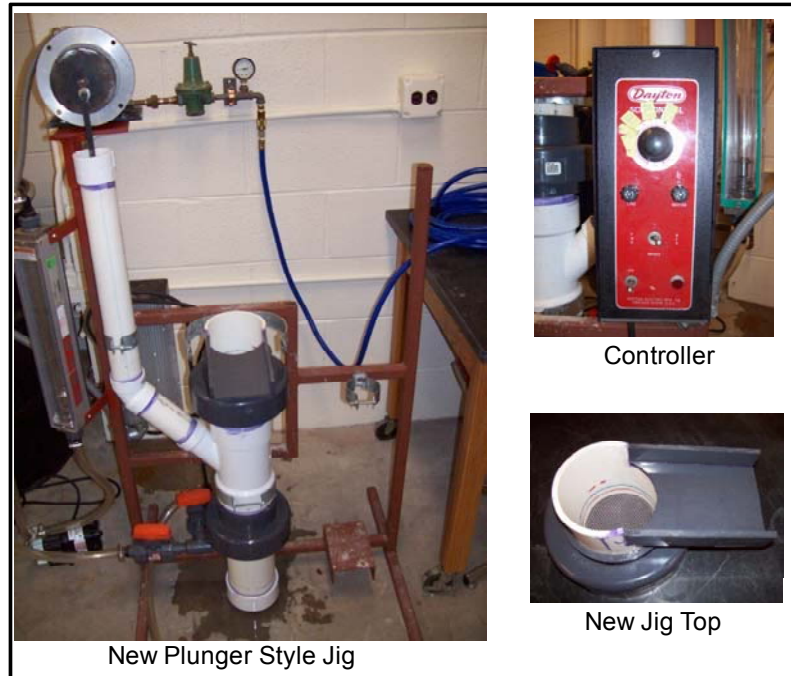
Figure 17. Plunger Style Jig.

EXPERIMENTAL SETUP

The hutch flow rate and hutch fluid are two important parameters for the jigging process. As stated in the theoretical discussion, there may be an opportunity to increase the efficiency of dolomite removal by using an acid solution. This would require some sort of acid storage for the hutch water fluid. Figure 18 shows the complete experimental setup including plastic 55-gallon storage tanks. A magnetic chemical drive pump was connected to the storage tank using acid-resistant PVC valves and Tygon tubing. The recycle and valves were used to control the hutch water flow rate. An acid-resistant rotameter was calibrated to make it easy to set the hutch water flow rate. As for the collection tank, a plastic 55-gallon drum can be used when there is no concern that any fines may go out the overflow. Otherwise, 5-gallon buckets can be used to collect the overflow and determine fines lost.
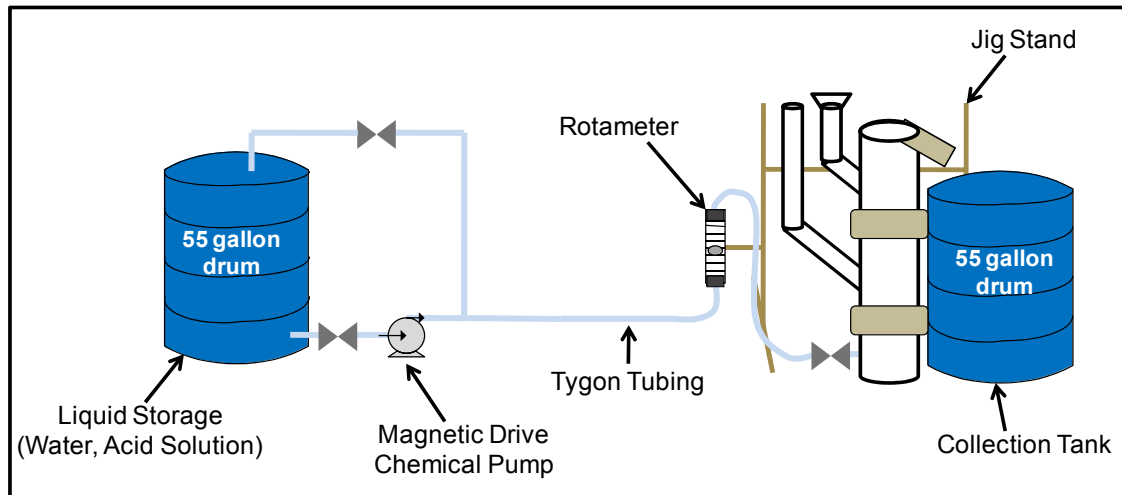
Figure 18. Complete Experimental Setup for Jig Testing.

EXPERIMENTAL PROCEDURE

Batch testing was used to determine how changing different jigging parameters affects jigging efficiency. Important jigging parameters are as follows:

1. Total jigging time
2. Jig bed depth
3. Hutch water flow rate
4. Pulsation stroke length
5. Pulsation rate

The first two parameters (jig bed depth and total jigging time) could be used later to calculate the feed rate and retention time for a continuous jigging process. Stroke length and pulsation rate are said to be two of the most important jigging parameters (Mukerjee and Mishra 2006). With a longer stroke length, hindered settling is the key separation mechanism due to the vastly different settling velocities of the different sized particles. In the following experiments, the feed was in a pebble form and had been sized by screening to 6.73mm by +3.36mm. A smaller stroke length was desired for this feed, as the key separation mechanism is initial differential acceleration. Initial differential acceleration occurs at the very beginning of the pulsation stroke (hence "initial" differential acceleration) and creates a separation due to differences in densities. Finally, the hutch water flow rate is the rate at which a constant flow of water is pumped up through the jig. The hutch water helps in the fluidization of the jig bed. When added at high enough rates, hutch water can be used to limit the effects of the suction stroke.

A batch testing procedure was developed and used for jig testing. Figure 19 shows the top piece of the jig. First, the hutch water flow rate was set using the calibrated rotameter. After the desired flow rate was reached, the pump was turned off. Next, the jig bed was filled to the desired height (approximately 335g of ore per inch of

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depth) with high-dolomite phosphate ore. The pump was then turned back on and a stopwatch was used to keep track of the total jigging time. While turning on and starting the pump, the pulsation motor was turned on with the pulsation rate set before starting. After the desired total jigging time was reached, the pulsation motor and pump were simultaneously shut off.

Before taking off the top piece of the jig, a valve at the bottom of the jig was used to drain it of water.
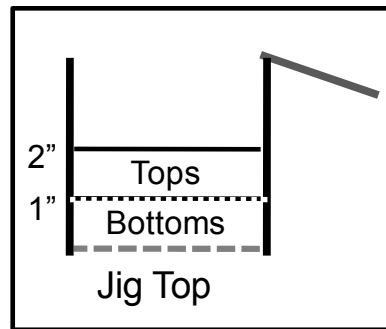
Figure 19. Diagram of Jig Top Piece.

Marks were made inside the jig top using a permanent marker to indicate the 1-inch and 2-inch levels. An angled spoon was then used to scrape off each layer starting at the top. For the initial testing, the layers were denoted as "tops" and "bottoms." Each layer was then dried and weighed in order to calculate weight recoveries. Next, representative samples were prepared (using a procedure similar to Figure 6) and analyzed for Mg content using atomic absorption spectrometry. The Mg results were then converted to MgO by multiplying by 1.658 (ratio of M.W. of MgO divided by M.W. of Mg).   The results could be plotted as weight recovery vs. % MgO.

Since the feed (-3/+6 mesh) was larger than the screen (10 mesh), no material was actually collected in the hutch. The jig bed stratified on top of the screen without any particles being pulled through the screen. This method of jigging is commonly referred to as "over the screen jigging."

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INITIAL JIG TESTING

Preliminary jig testing included quick experiments designed to determine how the jig was working and to identify any possible problems with the current jig and testing procedures. The first tests were designed to see how the pulsation rate and hutch water flow rates affected the efficiency of the jig. Jigging parameters that were kept constant are shown below in Table 3. The varied jigging parameters, pulsation rate and hutch water flow rate, are shown in Table 4.

Table 3. Constant Jigging Parameters for Preliminary Jig Testing.

Jigging time	2 min.
Liquid	Water
Jig Bed Depth	2"
Surfactant	None
Feed	3×6 mesh high-dolomite phosphate ore

Table 4. Varied Jigging Parameters for Preliminary Jig Testing.

Trial	Pulsation Rate	Hutch Water Flow Rate
T1	85 pulse/min.	1 gpm
T2	85 pulse/min.	2.5 gpm
T3	290 pulse/min.	1 gpm
T4	290 pulse/min.	2.5 gpm

The results from these tests are shown below in Table 5. It is apparent that at higher pulsation rates a better separation is achieved. It should be noted that there was a somewhat wide variation of % MgO in the feed. This is due to the fact that a somewhat coarse (-3/+6 mesh) pebble-size feed was used, which can result in sampling error.

Table 5. Results from Hutch Water Flow and Pulsation Rate Testing.

	T1		T2		T3		T4	
	% MgO	Wt. %	% MgO	Wt. %	% MgO	Wt. %	% MgO	Wt. %
Tops	4.05	57.7	2.65	60.3	3.80	56.0	4.06	61.6
Bottoms	3.08	42.3	2.07	39.7	1.97	44.0	1.94	38.4
Calc. Feed	3.64	100.0	2.42	100.0	2.99	100.0	3.25	100.0

Results can also be shown graphically in a plot of cumulative weight recovery vs. % MgO. The weight recovery is calculated by taking the layer closest to the screen and adding subsequent layers. A weight recovery of 100% corresponds to the % MgO in the total feed. For these tests there were only two layers, "tops" and "bottoms," so the weight recovery curve is simply a straight line. Figure 20 shows that a better separation was accomplished at higher pulsation rates (T3 and T4). The wide variation in MgO feed

concentration can also be seen in this graph. Plotting total weight rejected vs. % of total MgO will help normalize the results.
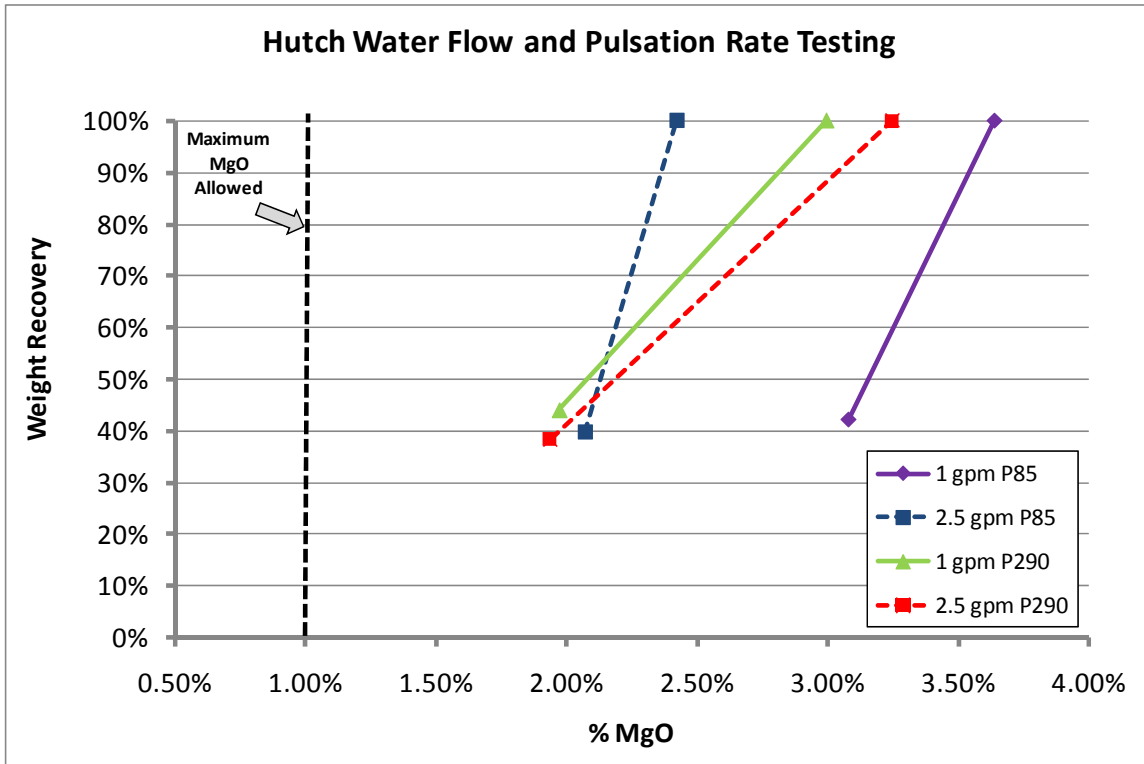
Figure 20. Jigging Results for Hutch Water Flow and Pulsation Rate Testing.

Figure 21 shows the plot of weight rejected vs. % of total MgO for the preliminary pulsation rate and hutch water flow tests. This plot was made by taking the topmost layer and adding subsequent layers until the screen was reached (i.e. weight rejection). This weight rejection was plotted against % of total MgO in the feed. Thus at 100% weight rejection there will be 100% of total MgO. The two high pulsation rate tests (T3 and T4) rejected a higher percent of the total MgO at a weight rejection of 60%. It can also be seen from this graph that the two high pulsation rate tests and the two low pulsation rate tests practically fell on top of each other, with the two high pulsation rate tests giving significantly better results than the low pulsation rate tests. This would indicate that the pulsation rate has a greater effect on the separation than the hutch water flow rate.

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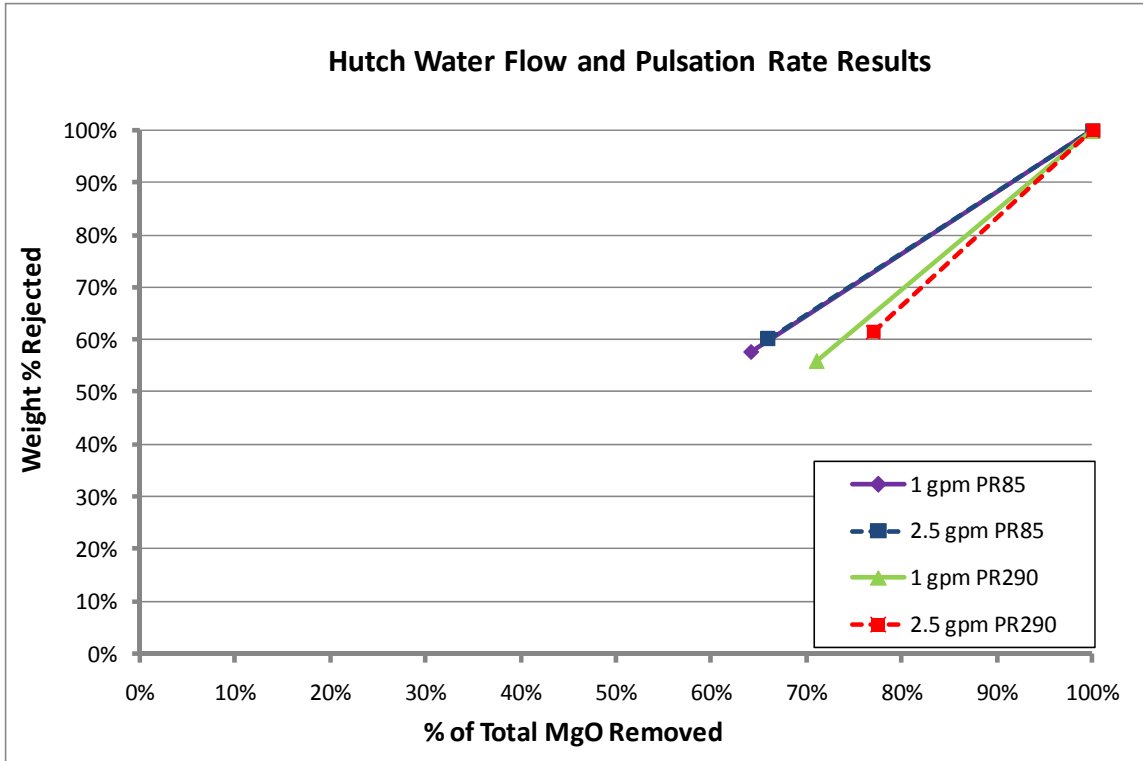
Figure 21. Jigging Results for Preliminary Pulsation Rate and Hutch Water Flow Tests.

MODIFYING JIG TESTING PROCEDURES

After analyzing the preliminary jig tests, it was apparent that using only two layers ("tops" and "bottoms") did not provide enough insight on the quality of separation. More than two points were desired in order to get a better idea of the particle stratification through the jig bed.

It was determined that separating the particle bed into four layers would give a more detailed look into particle stratification and MgO removal throughout the jig bed. Figure 22 shows the new layers designated as Zone 1, Zone 2, Zone 3, and Zone 4. Zone 1 is located on top of the screen and Zone 4 is the top layer of the particle bed.
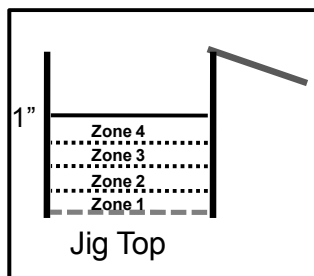
Figure 22. Diagram of Jig Top Piece.

JIG TESTING – VARYING PULSATION RATES

PARAMETERS

Pulsation rate is the second most important parameter in the jigging process behind jigging time (Mukerjee and Mishra 2006). In any jigging process there is some optimal pulsation rate (frequency). The following tests were performed with the goal of determining the optimum pulsation frequency for the jigging process used to separate dolomite from apatite. The jigging parameters kept constant are listed below in Table 6. The pulsation rates tested were 100, 200, and 300 pulse/min. Each test was done in triplicate to check for reproducibility.

Table 6. Constant Jigging Parameters for Pulsation Rate Testing.

Jigging time	1 min.
Fluid medium	Water
Bed depth	1"
Surfactant	None
Hutch water flow	1 gpm
Feed	3×6 mesh high-dolomite phosphate ore

RESULTS

The results from the pulsation rate studies are shown below in Table 7. The higher pulsation rates (200 and 300 pulse/min.) showed a significantly better separation than the lower pulsation rate (100 pulse/min.). However, from this table it is not apparent whether a pulsation rate of 300 pulse/min. is better than a pulsation rate of 200 pulse/min.

The results were also plotted as a graph of weight % rejected vs. % of total MgO removed, which is shown in Figure 23. This figure shows that tests at the higher pulsation rates of 200 and 300 pulse/min. gave better results than the tests at 100 pulse/min. Ideally, it is desired to be able to remove a large amount of the MgO while rejecting a small amount of the total weight.

The results from the pulsation rate jigging tests showed that the higher pulsation rates of 200 and 300 pulse/min. gave a better separation than the lower pulsation rates. The tests run at 200 pulse/min. appeared to be similar to, or better than, that of the test using a pulsation rate of 300 pulse/min. Furthermore, when attempting to use even higher pulsation rates (400 or 500 pulse/min.), the fluid flow became chaotic and there was no longer a uniform pulse across the jig bed. For this reason a pulsation rate of 200 pulse/min. was assumed to be the optimum for this set of jigging parameters.

Table 7. Results from Pulsation Rate Jigging Tests.

Pulsation Rate – 100 Pulse/Min.						
	T1		T2		T3	
	% MgO	Wt. %	% MgO	Wt. %	% MgO	Wt. %
Zone 4	3.71	20.92	4.18	20.58	4.04	20.73
Zone 3	3.89	25.47	2.88	26.27	3.51	25.53
Zone 2	3.64	26.58	3.70	29.06	2.88	26.64
Zone 1	2.82	27.03	3.14	24.09	2.88	27.09
Calc. Feed	3.49	100.00	3.45	100.00	3.28	100.00

Pulsation Rate – 200 Pulse/Min.						
	T1		T2		T3	
Zone 4	3.85	16.96	3.83	20.58	3.98	20.92
Zone 3	4.09	19.99	4.07	26.27	4.48	25.47
Zone 2	4.18	29.01	3.57	29.06	3.11	26.58
Zone 1	2.01	34.04	1.75	24.09	1.88	27.03
Calc. Feed	3.37	100.00	3.32	100.00	3.31	100.00

Pulsation Rate – 300 Pulse/Min.						
	T1		T2		T3	
Zone 4	4.06	15.19	3.59	18.46	4.29	25.51
Zone 3	4.37	17.10	3.89	24.81	3.67	23.55
Zone 2	4.16	28.56	3.44	30.61	3.99	25.82
Zone 1	2.30	39.15	1.57	26.11	1.80	25.12
Calc. Feed	3.45	100.00	3.09	100.00	3.44	100.00
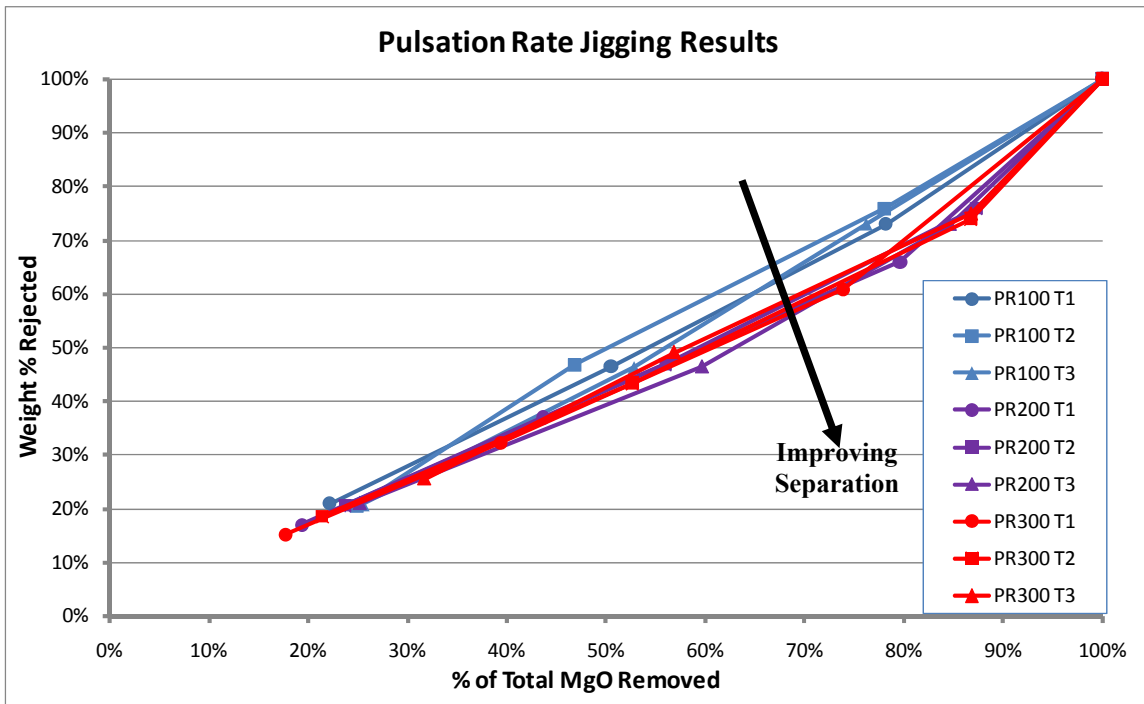
Figure 23. Jigging Results for Pulsation Rate Tests.

The jigging process seemed to work well for separating out about 25-30% (Zone 1) of the phosphate while the remaining 75-80% (Zones 2, 3, and 4) showed very little variation in % MgO. It is believed that this is due to the density differences described in the previous discussion about density studies. Figure 24 shows the actual samples from one of the 200 pulse/min. pulsation rate tests. This photograph shows a large percent of the dark apatite was concentrated into Zone 1, and to a lesser extent in Zone 2. This was to be expected, as our density studies showed that the dark apatite pebbles had the greatest density at approximately 2.8 g/cm^3 while the light gray apatite and dolomite pebbles had similar densities at around 2.5 g/cm^3. The underlying problem hindering the efficiency of gravity separation processes is that the light gray apatite and the light yellow rough dolomite pebbles have very similar densities. In order for jigging (or any other gravity separation process) to be a feasible method for removing dolomite from high-dolomite phosphate ores, we must increase the density difference between the light gray apatite and the porous yellow dolomite pebbles.

Figure 24. Samples from 200 Pulse/Min. Pulsation Rate Test.

JIG TESTING – ACID SOLUTION FLUID MEDIUM
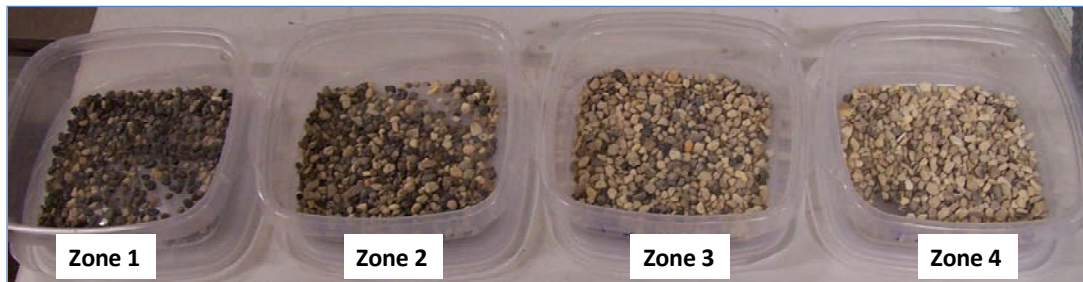
For a jigging process to work efficiently there must be a large enough density difference between the dolomite and apatite pebbles. The next set of tests was designed to investigate the hypothesis that using an acid solution will decrease the apparent density of the dolomite pebbles due to the reaction producing CO_2 on the surface of the dolomite pebbles.

PARAMETERS

The following tests were run using the jigging parameters shown below in Table 8. The main difference is that a 2% (by volume) sulfuric acid solution was used as the jigging fluid medium. A pulsation rate of 200 pulse/min. was used because it showed the best results from the previous pulsation rate studies.

Table 8. Parameters Used for Acid Solution Jigging Tests.

Jigging time	1 min.
Pulsation rate	200 pulse/min.
Fluid medium	2% vol. sulfuric acid solution
Bed depth	1"
Surfactant	None
Hutch water flow	1 gpm
Feed	3×6 mesh high-dolomite phosphate ore

RESULTS

Results from the acid solution jigging tests are shown below in Table 9. The results were plotted in a graph of weight % rejected vs. % of total MgO removed and is shown below in Figure 25. Also plotted on this graph are the results for the 200 pulse/min. pulsation rate tests done with a water fluid medium.

Table 9. Parameters Used for Acid Solution Jigging Tests.

Pulsation Rate 200 Pulse/Min. – 2% Acid Solution				
	T1		T2	
	% MgO	% Wt.	% MgO	% Wt.
Zone 4	3.49	17.06	4.02	22.91
Zone 3	3.17	25.39	3.85	26.97
Zone 2	3.74	28.69	3.18	22.00
Zone 1	1.95	28.87	2.04	28.12
Calc. Feed	3.04	100.00	3.23	100.00
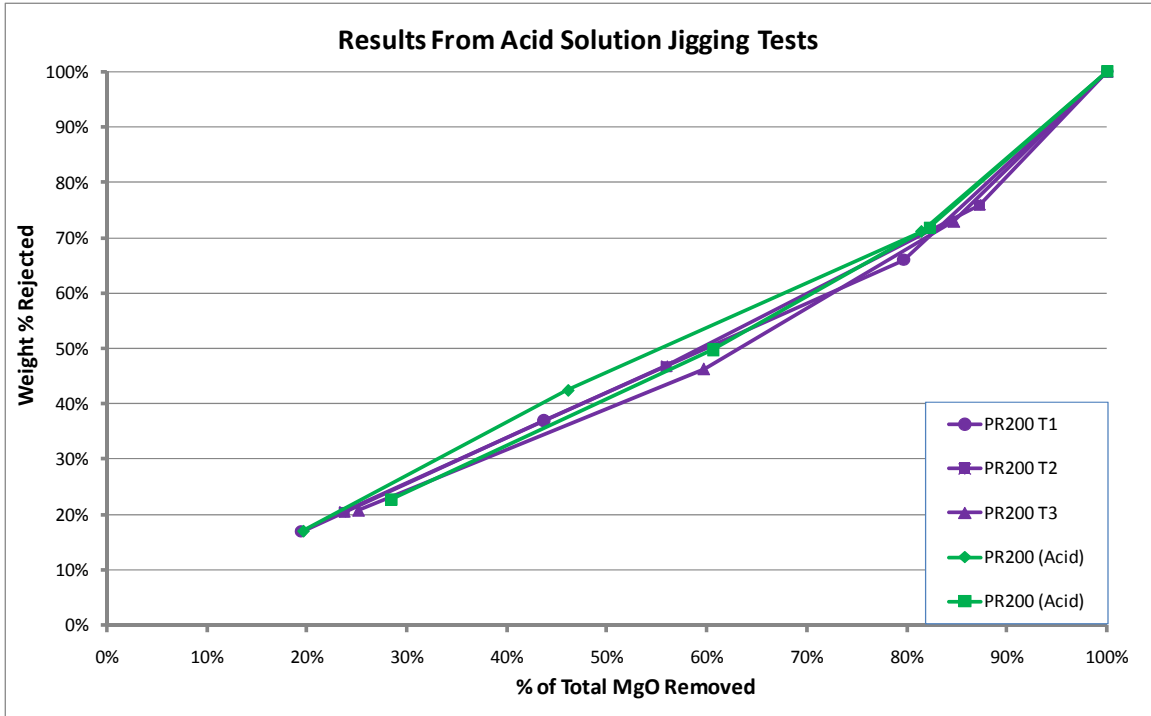
Figure 25. Jigging Results for Acid Solution Jigging Test.

The results from the acid solution jigging tests did not show any improvement over those from the water fluid medium. In fact, the results indicate that the acid solution may actually slightly decrease the efficiency of the separation. This is most likely due to the fact that the CO_2 bubbles generated by the acid attack on the dolomite did not stick to the surface of the pebble. It could be that the CO_2 bubbles simply act in decreasing the density of the fluid around the pebble which would in turn decrease the efficiency of the separation as described by the concentration criterion (Equation 2). This means that in order for the CO_2 bubbles to effectively decrease the apparent density of the dolomite pebbles, a surfactant must be used to make the bubbles stick to the surface of the pebble.

JIG TESTING – ACID SOLUTION AND POLYVINYL ALCOHOL (PVA)

Previous studies done by El-Midany (2004) have shown that polyvinyl alcohol (PVA) can be used to coat the dolomite pebbles and keep the CO_2 bubbles on the surface of the dolomite pebbles. The following experiments were designed to investigate how using PVA as a surfactant affects the efficiency of the jigging process to separate dolomite form apatite in high-dolomite phosphate ore.

PARAMETERS

A 3% PVA solution was used to coat the high-dolomite phosphate pebbles for the following test. The pebbles were coated by immersion in a beaker containing a 3% PVA solution followed by a sieve to remove excess PVA solution. The constant jigging parameters for the PVA surfactant jig tests are shown below in Table 10.

Table 10. Parameters Used for PVA Surfactant Jigging Tests.

Jigging time	1 min.
Pulsation rate	200 pulse/min.
Fluid medium	2% vol. sulfuric acid solution
Bed depth	1"
Surfactant	3% PVA solution
Hutch water flow	1 gpm
Feed	3×6 mesh high-dolomite phosphate ore

RESULTS

Results from the PVA surfactant jigging test are shown below in Table 11. The results were plotted in a graph of weight % rejected vs. % of total MgO removed and are shown below in Figure 26. Also plotted on this graph are the results for the 200 pulse/min. pulsation rate tests done with a water fluid medium and the jigging tests using an acid solution fluid medium.

Table 11. Results from PVA Surfactant Jigging Tests.

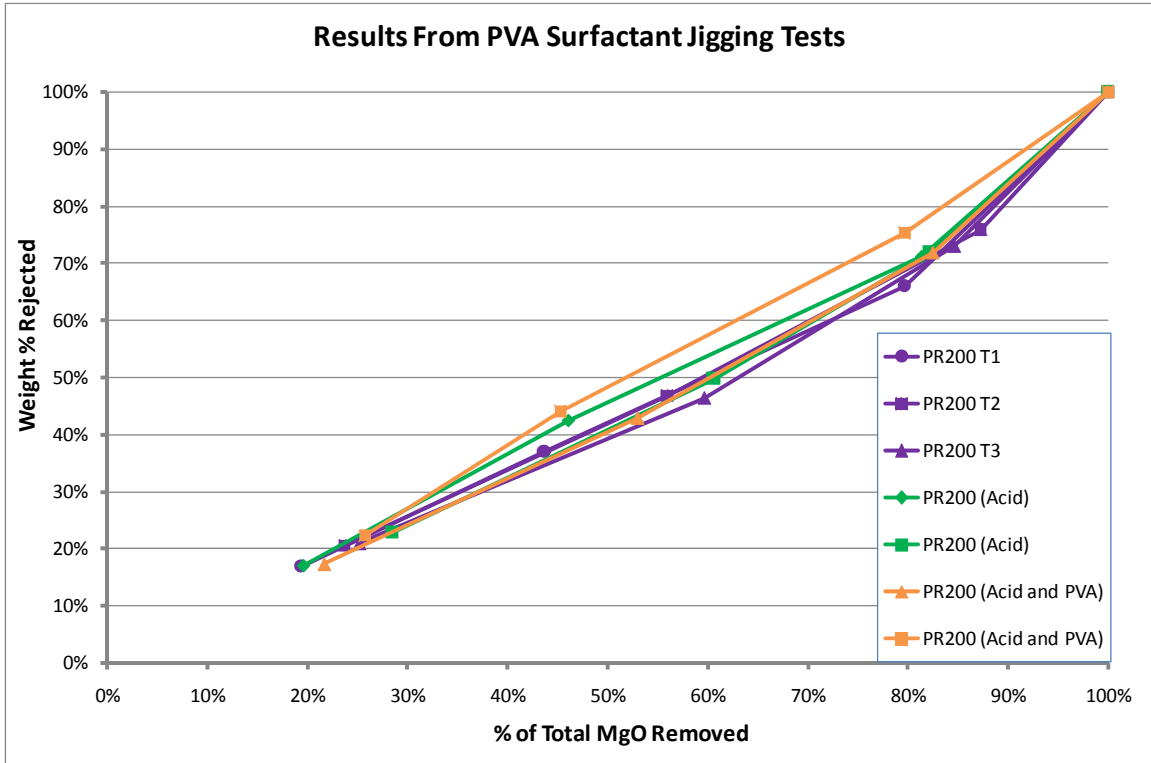| Pulsation Rate – 200 Pulse/Min. – 2% Acid – PVA				
	T1		T2	
	% MgO	% Wt.	% MgO	% Wt.
Zone 4	3.88	17.21	3.99	22.34
Zone 3	3.77	25.62	3.10	21.76
Zone 2	3.15	28.95	3.81	31.18
Zone 1	1.91	28.22	2.84	24.73
Calc. Feed	3.08	100.00	3.46	100.00

Figure 26. Jigging Results for PVA Surfactant Jigging Test.

The 3% PVA surfactant showed no improvement over the jigging tests using a water solution fluid medium and no surfactants. One PVA surfactant test actually showed a decrease in jigging efficiency. The PVA may have acted in increasing the viscosity within the particle bed, which would in turn hinder particle movement and decrease the efficiency of the jigging process.

El-Midany (2004) showed positive results with his reactive flotation process that used PVA as a surfactant. It was noted that an adequate amount of time is needed for the acid to react with the dolomite and produce CO_2 bubbles. The one-minute jigging time may not have been long enough to allow the reaction to produce enough bubbles on the surface of the dolomite pebbles to effectively decrease the apparent density of the dolomite pebbles.

DENSE FLUID JIGGING PROCESS

Using a dense fluid as the jigging fluid medium would increase the concentration criterion. The only problem with using dense fluids is that typically, as the density of a fluid is increased, the viscosity also increases. High-viscosity fluids hinder particle movement and decrease the efficiency of the jigging process. This means a way must be found to make a dense fluid without dramatically increasing the viscosity. Creating a salt solution could increase the density of the jigging fluid without significantly increasing the viscosity.

JIGGING TEST – CaCl$_2$ DENSE FLUID JIGGING

Parameters

A 50% (by weight) calcium chloride solution was used for the following heavy fluid jigging tests. The CaCl$_2$ solution had a specific gravity of 1.36. Since we didn't want to use a large amount of CaCl$_2$ for preliminary heavy fluid jig testing, we designed a smaller jig which would considerably cut down on the amount of fluid needed for each trial. Figure 27 shows a photo of the new "small plunger style" jig. This jig has a "U" shape and is made out of two-inch PVC pipe.

Figure 27. Small "U" Shaped Jig.

Using a smaller jig meant that it was necessary to use a smaller-sized feed in order for the jigging process to work effectively. A smaller-sized feed would also greatly reduce any sampling error that would be caused by large pebble-sized feeds. Table 12 shows the jigging parameters used for the $CaCl_2$ heavy fluid jigging tests. It should also be noted that one test was run using a water fluid medium and was used for comparison with the results from the $CaCl_2$ heavy fluid jigging test.

Table 12. Parameters Used for CaCl₂ Heavy Fluid Jigging Tests.

Jigging time	1 min.
Pulsation rate	200 pulse/min.
Fluid medium	50% wt. CaCl₂ solution
Bed depth	1" or approximately 100 g
Surfactant	None
Hutch water flow	0 gpm
Feed	-6 mesh high-dolomite phosphate ore

Results

The results from the heavy fluid jigging test are shown below in Table 13. One major difference between these jigging tests and the previous jigging tests is that the use of -6 mesh feed allowed particles to go through the screen. This meant that an "over-the-screen" jigging process was no longer being used, but instead a more common jigging process which allows the consolidation trickling mechanism to pull small dense pebbles through the screen. The pebbles that go through the screen are collected as the "hutch" product. The results were also plotted as weight % rejected vs. % of total MgO removed and are shown below in Figure 28. Also plotted on this graph are the results from the 200 pulse/min. pulsation rate tests.

Table 13. Results from CaCl₂ Heavy Fluid Jigging Tests.

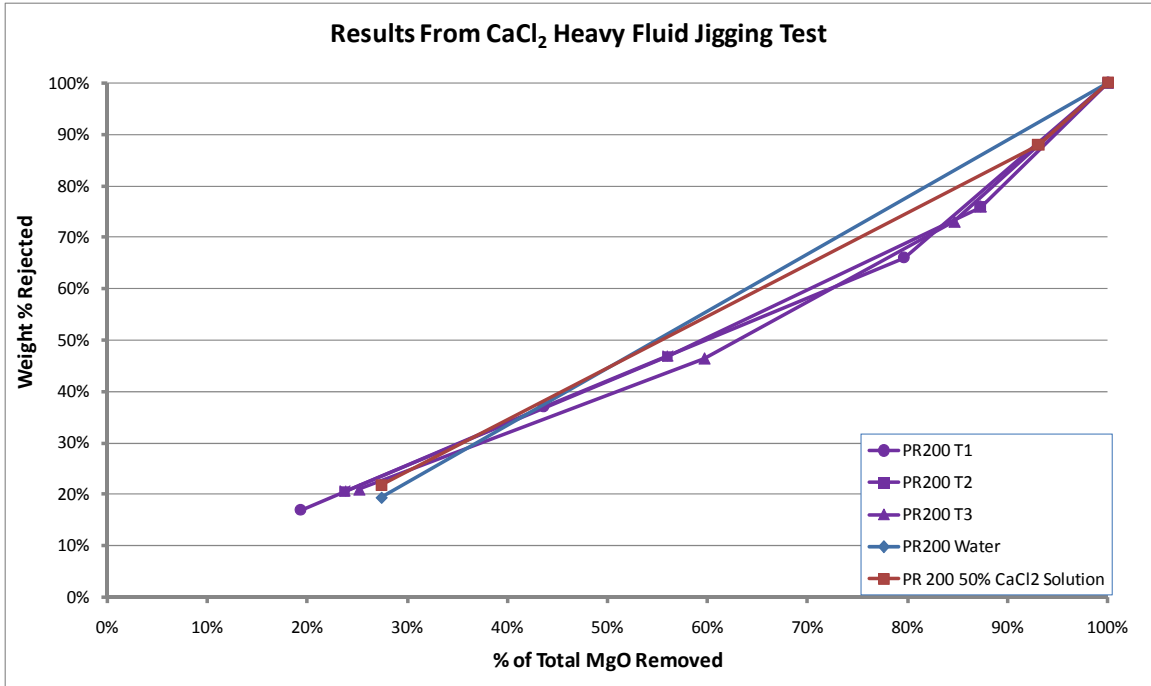| Pulsation Rate – 200 Pulse/Min.				
	T1 (Water)		T2 (CaCl₂ Solution)	
	% MgO	% Wt.	% MgO	% Wt.
Tops	2.44	19.40	1.82	21.88
Bottoms	1.56	80.60	1.44	66.01
Hutch			0.83	12.10
Calc. Feed	1.73	100.00	1.45	100.00

Figure 28. Jigging Results for CaCl₂ Heavy Fluid Jigging Test.

Using a CaCl₂ heavy fluid seemed to increase the quality of the separation compared to previous tests done with a 200 pulse/min. pulsation rate, although it is hard to compare the results due to the fact that there are fewer data points for the two tests done on the new small plunger jig. The water test done on the small jig also showed promising results. At the 20% weight rejection mark, this test showed a removal of approximately 28% of the total MgO, which was the best out of all the jigging tests done to that point.

ADDITIONAL JIGGING TESTS – CaCl₂ DENSE FLUID

Parameters

Since the previous heavy fluid jigging tests using a CaCl₂ solution were inconclusive, more tests were needed before deciding whether or not to move forward in developing a heavy fluid jigging process. The constant jigging parameters were unchanged from those shown in Table 12. Two tests were done using a 50% (by weight) CaCl₂ heavy fluid solution and two tests were completed using water.

Results

The results from the heavy fluid and water jigging test are shown below in Table 14. The results were also plotted as weight % rejected vs. % of total MgO removed and

are shown below in Figure 29. Finally, the heavy fluid jigging tests were plotted alongside the results from the 200 pulse/min. pulsation rate tests in Figure 30.

Table 14. CaCl2 Heavy Fluid and Water Jigging Test.

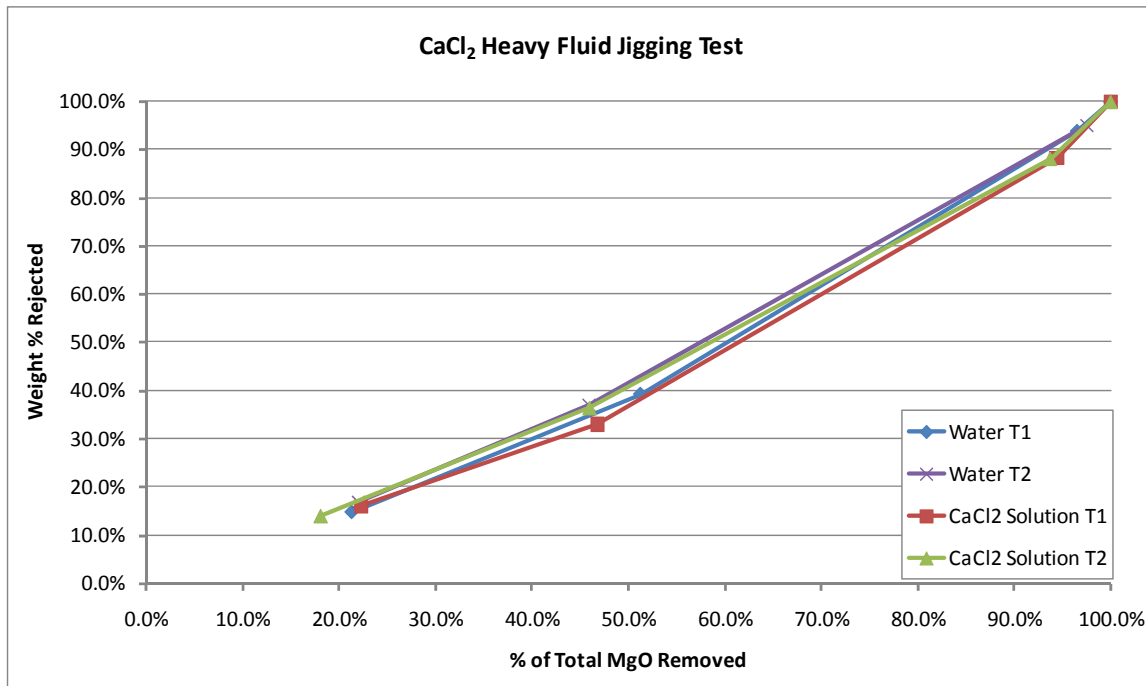| Pulsation Rate – 200 Pulse/Min.								
	Water – T1		Water – T2		CaCl$_2$ Solution – T1		CaCl$_2$ Solution – T2	
	% MgO	Wt. %	% MgO	Wt. %	% MgO	Wt. %	% MgO	Wt. %
Tops	2.09	14.8	1.79	16.9	1.71	16.1	1.68	14.0
Middle	1.77	24.5	1.63	20.0	1.78	17.0	1.62	22.4
Bottoms	1.20	54.6	1.22	58.2	1.06	55.4	1.20	51.8
Hutch	0.83	6.1	0.68	4.9	0.60	11.5	0.69	11.8
Calc. Feed	1.45	100.00	1.37	100.00	1.23	100.00	1.30	100.00

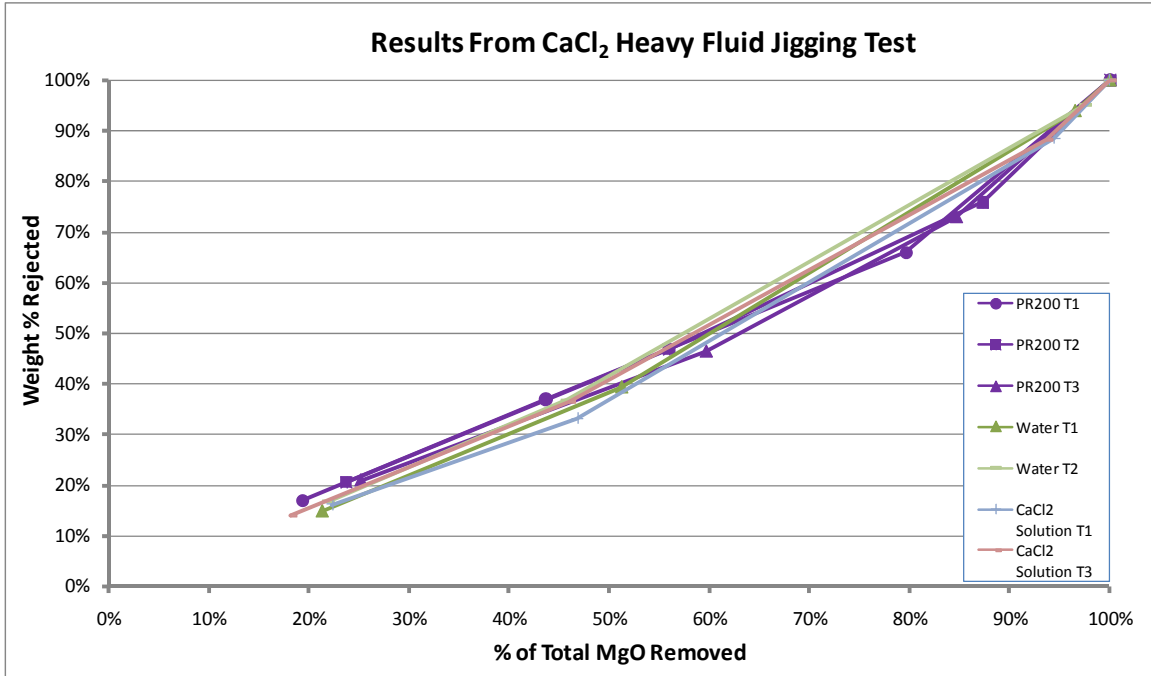**Figure 29. CaCl$_2$ Heavy Fluid Jigging Results.**

Figure 30. CaCl₂ Jigging Results Plotted with 200 Pulse/Min. Jigging Tests.

The best results from all the jigging tests came from the CaCl$_2$ solution T1 jigging test performed on the small "U" shaped jig. This jigging scenario removed approximately 43% of the MgO present while rejecting 30% of the total weight. This scenario also achieved a weight recovery of 66.9% at approximately 0.98% MgO. It was also noticed that using the CaCl$_2$ solution resulted in a significant increase in the amount of "hutch" product collected compared to the experiments using water.

When compared to the previous 200 pulse/min. rate tests performed on the larger plunger style jig, all tests done on the smaller "U" shaped jig gave better results (as shown above in Figure 30). The main difference between the two sets of experiments (besides using the CaCl$_2$ solution for two tests) was that the experiments performed on the small "U" shaped jig were carried out using a finer-size fraction (-6 mesh). The use of a finer-size fraction feed material allowed the consolidation trickling mechanism to pull the fine dense particle through the screen and into the "hutch" product. More importantly, the "hutch" product contained the least amount of MgO when compared to all other zones.

CONCLUSIONS

Physical separation of dolomite from phosphate pebble can be accomplished at a coarse size without crushing or grinding the material. This is possible because the dolomite pebbles and the phosphate pebbles are sufficiently liberated from each other. Analysis of a high-dolomite phosphate pebble sample showed that the dolomite was preferentially concentrated in the coarse fraction, and so a large fraction of it can be rejected by sizing the material.

Analysis of the individual pebbles showed that there were three distinct types: dark-colored pebbles that were relatively high-density apatite, light gray pebbles that were lower-density apatite, and yellow, porous pebbles that were dolomite.

Experiments with a custom-built jig showed that the dark apatite pebbles were sufficiently dense that they could be separated by jig separation using only water as the jig fluid. This allows for a relatively simple first step of upgrading the material.

It was determined that the use of acid to generate gas bubbles on the surface of the dolomite particles did not sufficiently reduce the density of the dolomite pebbles to improve their removal by the jig. This was probably due to the fact that the gas bubbles did not adhere to the surface of untreated dolomite particles. Treating the dolomite with polyvinyl alcohol did help to retain the gas bubbles on the dolomite surfaces, but it slowed the reaction rate sufficiently that there was an insufficient generation of gas during the one-minute processing time used in the jig.

A new approach to improving the ability of a jig to remove dolomite from apatite has been tested. This consists of raising the density of the jig working fluid to improve the value of the concentration criterion and make separation easier. The results of this approach are very promising, and there are plans to pursue it further.

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