IBP1145_15

PUMPING FOAMY SLURRIES- CHEMICAL TREATMENT FOR OPTIMIZED OPERATION

Ana F. Lara[1], Jay P. Chapman[2], Alisson M. Vidal[3], Rafael C. Lima[4], Daniel R. Sá[5], Paulo J. Bruzzi[6]

Abstract

The foam generated in iron ore flotation is usually pumped via pipeline to a tailings reservoir. However, pumping foamy slurry reduces the system efficiency and also increases maintenance costs (pump wear). Quartz, the main waste mineral contained in iron ore, is generally floated by means of cationic reverse flotation at alkaline pH. In this process the ether-amine is used as a collector and as a foaming agent. These functions are due to amine dissociation in aqueous solution, in which the molecular and ionic species co-exist. In this chemical equilibrium, acidity favors the dissociated form and alkalinity favors the molecular form. The work focuses on reducing aeration of slurry, targeting an improvement in tailings pipeline operation by improving centrifugal pump performance. Initially, alternatives were analyzed to reduce foam stability, through slurry neutralization – pH 7.5. After neutralization, bubbles still exist, but with less stability. After acid dosing, high pressure water is sprayed on the treated slurry. The water spray to reduce bubble stability is a complementary treatment to neutralization. The lab tests show reduced foaming factor, when the treatment is used (neutralization combined with water spray).

1. Introduction

Many iron ore processing plants in Brazil use cationic reverse flotation as the primary method of ore concentration. During flotation, the separation between silica and iron ore is possible by circulating a flow of air through an aqueous suspension containing the two species. The hydrophobic particles are collected by the air bubbles and the hydrophilic particles remain in the suspension. This process requires the production of foam, so that a big area air-liquid interface can be created and can remain stable. Thus, to reach satisfactory results, a foaming agent and other reagents are used to enhance the separation process

The work focuses on reducing aeration of slurry, targeting an improvement in tailings pipeline operation by improving centrifugal pumps performance.

1.1. Pumping Foamy Slurry

During flotation, the fine tailing particles are collected by the air bubbles and taken to the surface. The foam generated in flotation cells consists of fine particles with small air bubbles

The floated tailings generated are usually pumped via pipeline to a tailings reservoir. Most often, depending on the distance between the processing plant and the tailings reservoir and the geometry of the terrain, trains of centrifugal pumps are used to move the slurry.

Pumping foamy slurry is difficult due to problems caused by air presence in centrifugal pumps. The efficiency of the pumping system is impaired due to reduced pump head. This lower head reduces the throughput and pumping efficiency; it also increases vibration, wear, noise, heat and cavitation. In addition, it increases maintenance costs.

---

[1] Chemical Engineer - AUSENCO
[2] Sr. VP Master, Engineering – AUSENCO
[3] Mechanical Engineer – AUSENCO
[4] Mechanical Engineer – AUSENCO
[5] Technical Designer – AUSENCO
[6] Master, Mechanical Engineer - AUSENCO

1.2. Typical Problems in Pumping Foamy Slurry

Foamy slurries generally contain a large amount of solids particles and air bubbles. The air inside the suspension is equivalent to a fluid with high vapor pressure. Consequently, the NPSH available in the foamy slurry is too low, with vapor pressure value near atmospheric pressure.

Therefore, the foamy slurry requires extra pumping energy due to the foam, passing through the pump impeller.

Some measures can be taken to reduce the impact of foam in the pump, for example: use low NPSH impellers, increase the pump suction diameter, which can induce pre-rotation and shear the foam in the pump suction, helping handling it. However, these methods are not always enough.

One of the ways to detect a problem in the system is to control the feed tank overflow. If the tank is continually overflowing, it is a sign that the pumps are having trouble transporting the foam. Excess vibration also indicates a system problem.

The work focuses on reducing aeration of slurry, targeting an improvement in tailings pipeline operation by improving centrifugal pump performance.

1.3. Flotation Reagents – Foam Stability

The operational variables of flotation are regulated by the ore characteristics. Parameters as: reagents, pH, temperature, slurry properties, among others, must be carefully adjusted to a more efficient process.

The reagents are organic and inorganic compounds used to control the interface characteristics. The choice of reagent influences air bubbles and foam characteristics, whose control is extremely important to the process optimization in a flotation plant.

The foaming agents are surfactants, reducing the interfacial tension, and its molecular form concentrates at the liquid / gas interface thus reducing the surface tension, and giving foam interlayer film elasticity.

The bubbles' stability is possible due to the electrostatic repulsive strength between the polar radicals of the surfactant molecules, and at the same time Van der Waals forces attract them by pressure difference, as can be seen in the Figure 1 below:

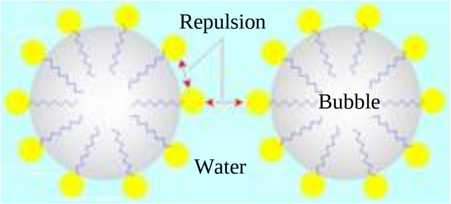

Figure 1. Repulsive forces maintains bubble stability

Quartz, the main waste mineral present in iron ore, normally is floated by means of cationic reverse flotation at pH 10.5. In this process an ether-amine is used as a collector and as a foaming agent.

The amines, at pH between 10 to 11, are used as quartz collectors and foaming agents. These functions are due to amine dissociation in aqueous solution, in which the molecular and ionic species co-exist. In this chemical equilibrium, acidity favors the dissociated form and alkalinity favors the molecular form.

The Equation 1 below shows the hydrolysis (or dissociation) of amine in aqueous solution.

$$R\text{-}O\text{-}(CH_2)_3\text{-}NH_2 \ + \ H^+ \leftrightarrow \ R\text{-}O\text{-}(CH_2)_3\text{-}NH_3^+.OH \text{ (eq. 1)} \tag{1}$$

The Figure 2 below shows the behavior of the species (molecular and ionic) in aqueous solution, according to the pH of the solution.

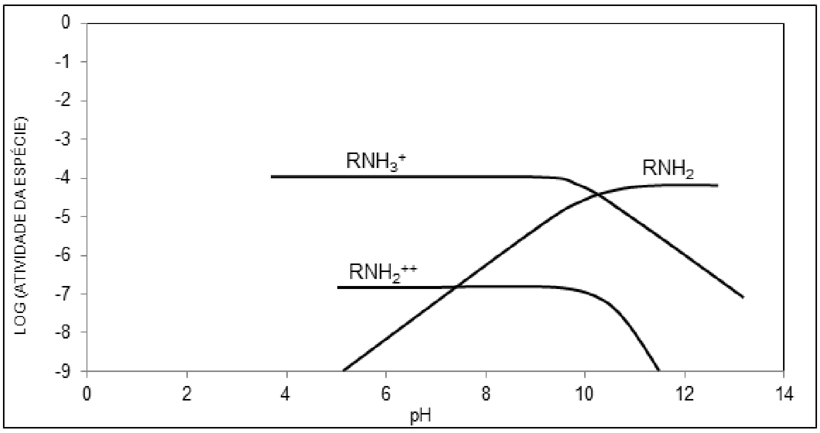

Figure 2. Species in solution according to the pH

The equation above (eq. 1) and Figure 2 show that an acid environment favors the dissociated form and a basic environment favors the molecular form. The condition that provides the equilibrium between the two species is located at pH 10.5, which is also the best pH condition for iron ore flotation.

The molecular species act as foaming agents, they concentrates at the liquid / gas interface thus reducing the surface tension, and giving foam interlayer film elasticity.

The work focuses on alternatives for tailings slurry neutralization, once neutralization disfavors molecular ether-amine species whose formation gives elasticity and bubble stability.

1.4. Alternative Reagents to Neutralization

Four alternatives were evaluated for flotation tailings slurry neutralization:

- Carbon dioxide (CO_2);
- Acetic acid (H_3CCOOH);
- Hydrochloric acid (HCl);
- Industrial acid.

Carbon dioxide

The carbon dioxide (carbonic acid gas – CO_2) is widely used for pH reduction because it is one of the safest and environmentally friendly solutions, compared to other acids.

Environmentally friendly, because when it dissolves in water, the carbon dioxide (CO_2) forms carbonic acid (H_2CO_3), which differently from the other mineral acids, avoids the excessive accumulation of salts, as chloride, sulfate, etc.

Safe application, because of the excessive acidification is almost impossible to happen when CO_2 is used, since its neutralization curve is nearly horizontal. Additionally, CO_2 gas is less corrosive.

Acetic acid – Weak acid

An acid is considered weak when its ionization in water is incomplete, in other words, at equilibrium both the acid and the conjugate base are present in solution. Weak acids have a smaller acid dissociation constant (K_a) and a larger logarithmic constant (pKa= - log Ka). The bigger K_a of an acid is, the more easily proton H+ is formed and the lower pH solution is.

Although acetic acid is a weak acid, which facilitates a better control of excessive acidification, it is corrosive to skin, eyes and mucous membranes.

Hydrochloric acid – Strong acid

A strong acid is one that completely ionizes (dissociates) in a solution, at constant temperature and pressure. In water, one mole of a strong acid HA dissolves yielding one mole of H+ (as hydronium ion H_3O+) and one mole of the conjugate base, A−. Essentially, none of the non-ionized acid HA remains.

As a strong acid, hydrochloric acid is extremely corrosive and requires special attention during its handling, besides the need of rigid operational control at the end point, because it can promote excessive acidification.

Industrial acid – Strong acid

The industrial acid is a compound used as a high performance inorganic coagulant, in the treatment of potable water, industrial effluents and sewage. It is a product made of iron oxide and sulfuric acid, so it is highly corrosive and measures must be taken to avoid contact with metal.

1.4. Foam Reduction

The main goal of the proposed solution is to reduce tailing stream foam before it arrives at the centrifugal pump suction nozzle.

After the neutralization, the bubbles continue to exist, but with less stability.

A widely used solution is the use of fan-shaped commercial nozzles to reduce foam at the top of the box. This solution has its effect maximized when the bubbles have lower stability so the air contained inside them can ascend and arrive at the feed tank surface (tall tank, with large residence time). Thereby, the water sprayed at the box can mechanically break the foam.

The water sprayed must have enough pressure to rupture the bubbles, but it cannot introduce excessive system turbulence.

The work proposes the optimization of the system by installation of water sprays over the troughs that arrive from tailings flotation to boxes at the top of the feed tank.

Figure 3 and Figure 4 show typical assemblies of foam reduction water sprays. Figure 3 shows the installation at the top of the tank and Figure 4 shows the installation at the overflow trough of the flotation cells and columns.

Figure 3. Spray on top of the tank.

Figure 4. Spray on top of the troughs.

2. Methodology

Initially, alternatives were analyzed for slurry neutralization.

Theoretical calculations were performed to all the alternatives (CO_2, H_3CCOOH e HCl), based on dissociation constants of the acids and gases absorptions.

For the industrial acid, data collected in bench tests was used, and the water spray efficiencies were also analyzed. Foam factors were measured, before and after the proposed treatments.

2.1 Methodology – Theoretical Calculations

The dissociation constants were the calculation basis for the alternatives (CO_2, H_3CCOOH e HCl). The following assumptions were used in the theoretical study:

- The solids are inert to the neutralization reaction, therefore only the reaction of the water in the slurry will be evaluated;
- Losses of efficiency in the reaction due to heat liberation or absorption were not considered;
- The slurry acts as an ideal solution.

Carbon dioxide

The most part of the carbon dioxide in aqueous solution is in the gas form. A small quantity of the carbon dioxide is converted to carbonic acid, according to Equations 2 and 3:

$$CO_2(g) + H_2O(l) \rightarrow CO_2(aq) \quad (2)$$

$$CO_2(aq) + H_2O(l) \rightarrow H_2CO_3(aq) \quad (3)$$

The solubility of gases in water is described by Henry's Law, which says at a constant temperature, the amount of a given gas that dissolves in a given type and volume of liquid is directly proportional to the partial pressure of that gas in equilibrium with that liquid, according to Equations 4 and 5:

$$CO_2(g) + H_2O(l) \rightarrow CO_2(aq) \quad (4)$$

$$[CO_2(aq)] = K_H{*}p\ CO_2(g)1 \quad (5)$$ [1]

The carbonic acid dissolved in water participates in both successive protons transfer equilibriums, according to Equations 6 and 7:

$$H_2CO_3(aq) + H_2O(l) \rightarrow H_3O^+(aq) + HCO^{3-}(aq) \qquad K_{a1} = 4{,}3 \times 10^{-7} \quad (6)$$

$$HCO^{3-}(aq) + H_2O(l) \rightarrow H_3O^+(aq) + CO_3^{2-}(aq) \qquad K_{a2} = 5{,}6 \times 10^{-11} \quad (7)$$

The conjugate base of H_2CO_3 in the first equation (HCO^{3-}), acts as an acid in the second equation. This ion then produces its own conjugate base CO_3^{2-}.

In higher values of pH, carbonic acid ionizes producing two protons, which then participate in the neutralization process. However, for pH values smaller than 9, only one proton is formed. Although the process of neutralization is continuous, from the chemical point of view it is possible to be distinguished in three phases.

Only 0.2% of the dissolved CO_2 is in the gas state. When the real value of H_2CO_3 is used in the place of $[H_2CO_3 + CO_2]$, the value of the equilibrium constant is according to Equations 8 and 9:

$$H_2CO_3(aq) + H_2O(l) \rightarrow H_3O^+(aq) + HCO^{3-}(aq) \qquad K_{a1} = 2 \times 10^{-4} \quad (8)$$

$$HCO^{3-}(aq) + H_2O(l) \rightarrow H_3O^+(aq) + CO_3^{2-}(aq) \qquad K_{a2} = 2 \times 10^{-8} \quad (9)$$

Acetic acid

Most of the acetic acid in aqueous solutions is in the molecular form. A small quantity of the acid ionizes, according to Equation 10:

---

[1] K_H is the Henry's law constant. CO_2 around CNTP (at 25°C (mol x L^{-1} x atm^{-1})), the $K_{H\text{-}CO_2}$ assumes 3.38 x 10^{-2}.

$H_3CCOOH \rightarrow H_3CCOO^- + H^+ \qquad K_{a1} = 1{,}74 \times 10^{-5}$ (10)

Hydrochloric acid

The dissociation of hydrochloric acid in water can be seen at the Equation 11 below:

$HCl(aq) \rightarrow Cl^- + H^+$ (11)

Considering that hydrochloric acid is a strong acid, the dissociation of the ions H+ and Cl- occurs with greater frequency compared with the formation of molecular HCl. It is possible to consider thus that the dissociation is complete, with no formation of HCl in the solution, only the coexistence of the ions H+ and Cl-.

2.2 Methodology – Bench Test

The slurry sample was collected in an iron ore mining plant located in the Quadrilátero Ferrífero – MG. It was originated from the flotation tailings and it was considered a representative sample for this study.

The process data of the flotation tailings used in the bench test can be found in Table 1

Table 1. Process data – Tailings

Property	Unit	Measurement
Solids concentration	% weight/weight	45
Solid specific gravity	t/m³	2.73
Slurry specific gravity	t/m³	1.19
Particle-size distribution	µm	-0.15+0.01
Foaming factor	%	1.5
pH	-	10.5

* The material of the test has 12.4% of Fe grade and 81.3% of SiO_2 grade.

Initially, the level of foam was confirmed using a test tube. Then, the slurry was transferred to a graduated beaker. Before the transfer, the dried beaker was weighted, and after the transfer it was weighted again to check the amount of slurry used in the test.

A pH indicator was installed in the beaker, so that the neutralization could be seen. Before the beginning of the test, pH was measured and its value was 10.5.

Once the system was ready, industrial acid was added with a pipette, until the pH reach the value of 7.5.

After neutralization, a mechanical agitator was installed in the beaker, where the slurry was agitated constantly for 10 minutes, simulating an agitated tank.

Figure 5 shows the settings of the bench test, with a mechanical agitator.

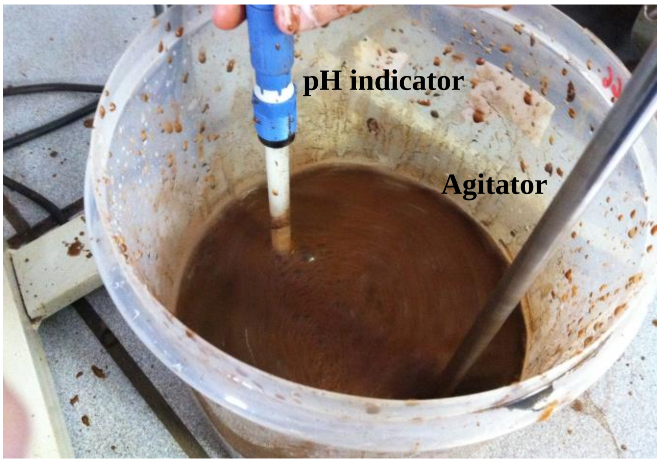

Figure 5. Laboratory test assembly

After 10 minutes, the material was transferred again to a beaker, were water was sprayed. The level of foam was measured again.

At the end of the test, the slurry was transferred to a weigh tray, which was transferred to hot plate until complete drying of the slurry. After that, the mass solids were again weighed.

3. Results

3.1. Results – Theoretical Calculations

The theoretical results are presented in the Table 2:

Table 2. Neutralization Dosage - CO_2, H_3CCOOH and HCl

Reagents	Dosage per hour	Stock - 15 days
CO_2	809 kg/h	291.4 t
H_3CCOOH [2]	1.03 m³/h	372.2 m³
HCl [3]	1.4 l/min	31.7 m³

3.2. Results – Bench tests

Neutralization and dosage

It was possible to verify through the performed tests that the consumption of the reagents were really similar. The result of the tests was a consumption of $0.13 l/m^3$ of industrial acid per cubic meter of water contained in the slurry.

When sizing the neutralization system, it is important that the dosage be made for the water present in the slurry, because the solids in the solution do not interfere significantly in the neutralization and must be excluded from the calculations.

For a more conservative design, it is interesting to adopt a higher design factor, above 1.2, which is commonly adopted in mining projects. As a suggestion, a factor of 1.35 could be used, once the information from suppliers is really restricted.

According to the tests, the dosage used for neutralization was $0.13 l/m^3$ per cubic meter of water. For purposes of system sizing, it is suggested to use a dosage of $0.15 l/m^3$ per cubic meter of water, to make sure that the neutralization will happen even if some variations of ROM quality and inherent operational variations occur.

Foam Reduction

The lab tests performed show reduced foaming factor, when the proposed treatment is used (neutralization combined with water spray).

4. Analysis

It can be concluded from the study presented:

4.1. Reagents alternatives

All the considered reagents CO_2, H_3CCOOH, HCl and Industrial acid caused a reduction of pH from 10.5 to 7.5.

Carbon dioxide – CO_2

Carbon dioxide is an inert gas, and generates a weak acid, so it is an environmentally friendly solution to the neutralization reaction.

It is an efficient solution for lowering the pH from 10.5 to 8.5-9.1, due to the dissociation constants, but to reach neutral pH the dosage increases significantly.

Another factor that interferes in CO_2 efficiency is the pressure. As it is a gaseous reagent, its solubility is proportional to the pressure of the gas in contact to the liquid, and the system operates by gravity, so it would be necessary to pressurize the slurry by recirculation, the dosage would then be made in a pressurized system.

Acetic acid - H_3CCOOH

Acetic acid is a weak acid and has good operation conditions, because it facilitates the control of excessive acidification.

However, it requires a large dosage to neutralize the solution because of its low dissociation constant.

---

[2] Acetic Acid Solution 48°

[3] Hydrochloric Acid Solution PA 37% w/w

Another disadvantage of using acetic acid is related to safety. In its pure form, acetic acid can form vapors that can cause health damage, in addition to being flammable. It is recommended that work be carried out at concentrations below 50%.

Hydrochloric acid- HCl

Hydrochloric acid is a strong acid and it completely ionizes favoring neutralization, plus a small quantity is necessary for the reaction. On the other hand, it is hard to work with it in neutral pH range, as it can easily cause excessive acidification.

Because it is highly corrosive, dangerous to health and the environment, hydrochloric acid needs to be handled with care. For field use, it is a not a very viable alternative, since it has strict environmental and safety controls.

Industrial acid

According to the results of the other alternatives, an inorganic coagulant option was studied, because it was already being used as a neutralizing agent in the owner’s processing plant.

The industrial acid showed satisfactory bench test dosage results.

4.2. Foam Reduction

The lab tests performed showed a satisfactory result regarding the rupture of the bubbles, when reaching pH 7.5, destabilizing the most part of them. After 10 minutes agitation, the bubbles were even more reduced.

The treatment with water spray helps to break the biggest superficial bubbles, which have smaller stability.

5. Conclusion

The work focuses on reducing aeration of slurry, targeting an improvement in tailings pipeline operation by improving centrifugal pumps performance. For that, a system of acid dosage for pH reduction was studied for neutralizing the flotation tailings.

Of the alternatives the most viable option in economic, technical and operational security terms was the industrial acid.

5.1. Proposed system

According to the positive results showed by the lab tests, the following project was proposed for the plant use. First, flotation tailings should be neutralized, followed by application of water sprays (in the trough and in the tank). The tank should have a residence time of 30 minutes and be constantly gently agitated.

From the results and considerations presented, it is possible to make some recommendations regarding the project:

- Due to the acid and corrosive material, all the storage and dosage equipment of the industrial acid coagulant should be made of non-metallic material, or must have the entire surface lined with an abrasion and corrosion resistant material;
- The industrial acid should be added to the slurry at a point close to the flotation cells, increasing the contact time between the coagulant and slurry, enhancing the effectiveness of the neutralization reaction;
- If possible, a gravity system should be designed;
- The storage tanks, as well as the troughs should be covered thus avoiding splashing;
- A pH indicator should be installed in the tanks in order to avoid super dosing;
- Keep the agitation with low rotation, enough to maintain the solids in suspension in order to not increase foaming;
- Build a tank with the largest residence time practical and keep the slurry level in the tank high so the air retained will have time to ascend and arrive at the surface, where it will receive the water spray.

5.2. Expected practical results

The proposed system is being installed in the iron ore processing plant in Quadrilátero Ferrífero – MG, where the samples used in the lab tests were collected

A reduction in the foaming factor from 1.5 to 1.3 is expected. A factor of 1.3 is the maximum foaming factor allowed at the pump suction, according to many centrifugal pump suppliers.

With the reduction of foaming factor, an improvement in the system efficiency is expected. Plus a reduction in pump power, vibration, wear, noise, heat and cavitation, will all reduce maintenance costs.

6. Bibliography

BARBATO, C., ANDRADE, M., FRANÇA, S., & LUZ, A. (s.d.). *ADSORÇÃO E QUANTIFICAÇÃO DE AMINAS EM EFLUENTES DE MINERAÇÃO.*

BENRETEM, A., BENIDIR, M., & CHALIB, R. (2010). *FACTORS INFLUENCING SLURRY RHEOLOGY.* World Pumps.

CAPPELINO, C., ROLL, D., & WILSON, G. (1992). DESIGN CONSIDERATIONS AND APPLICATIONS GUIDELINES FOR PUMPING LIQUIDS WITH ENTRAINED GAS USING OPEN IMPELLER/CENTRIFUGAL PUMPS. *Proceed the Ninth International Pump Users Symposium*.

CHAVES, A. (2006). *FLOTAÇÃO: O ESTADO DA ARTE NO BRASIL - TEORIA E PRÁTICA DO TRATAMENTO DE MINÉRIOS.* São Paulo: Signus Editora.

FALCUCCI, A. (01 a 04 de Setembro de 2013). BOMBEAMENTO DE ESPUMAS MINERAIS. *43º Seminário de Redução de Minério de Ferro e Matérias Primas e 14º Simpósio Brasileiro de Minério de Ferro.*

FALCUCCI, A., & TURRER, H. (01 a 04 de Setembro de 2013). THE EFFECT OF pH ON FROTH PROPERTIES. *43º Seminário de Redução de Minério de Ferro e Matérias Primas e 14º Simpósio Brasileiro de .*

HARRIS, D. (s.d.). *ANÁLISE QUÍMICA QUANTITATIVA.* LTC Editora.

VERAS, M. (2010). *INFLUÊNCIA DO TIPO DE ESPUMANTE NAS CARACTERÍSTICAS DE ESPUMA PRODUZIDA NA FLOTAÇÃO.* Recife.

WEIR MINERALS. (August de 2009). PUMPING FROTH. *Weir Minerals Technical Bulletin - #28.*