EVALUATION OF ALTERNATIVE REAGENTS FOR LIME IN LONG DISTANCE IRON ORE SLURRY PIPELINE[1]

Ana Cristina Calil Ramos Bragança[2]
Paulo Roberto Gomes Brandão[3]

Abstract

Two great concerns related to long distance slurry pumping systems are plug formation and sediment compaction. These problems are avoided in the Samarco Pipeline by adding lime. However, the presence of calcium ions in the process represents production losses, so alternative reagents were tested. Two organic coagulants and two flocculants were evaluated at dosages of 5, 100 and 300ppm by performing rheology, settling, penetration and angle of repose tests, before and after 24 hours under agitation. It was verified that a dosage of 300ppm of the organic coagulants affected the slurry properties likewise lime, so that they can replace it under this condition. Lower dosages do not result in coagulation or do not maintain the slurry coagulated with agitation, therefore they are considered insufficient. The changes generated by the flocculants in the slurry characteristics are not satisfactory since they do not minimize the high probability of plug formation. It was concluded that the aggregation state of the iron ore slurry must be changed by the coagulation mechanism in order to operate the system efficiently and safely.
Key words: Aggregation/dispersion; Pipeline; Lime alternative reagents.

AVALIAÇÃO DE REAGENTES ALTERNATIVOS PARA SUBSTITUIÇÃO DA CAL EM SISTEMA DE BOMBEAMENTO DE LONGA DISTÂNCIA DE POLPA DE MINÉRIO DE FERRO

Resumo

Duas grandes preocupações relacionadas a sistemas de bombeamento de polpa de longa distância são obstrução e compactação do sedimento. Estes problemas são evitados no Mineroduto Samarco através da adição de cal. Entretanto, a presença dos íons cálcio no processo representa perda de produção, logo, alguns reagentes alternativos foram testados. Dois coagulantes orgânicos e dois floculantes foram avaliados nas dosagens de 5, 100 e 300ppm através de testes de reologia, sedimentação, penetração e ângulo de repouso, antes e após 24 horas de agitação. Verificou-se que, quando dosados a 300ppm, os coagulantes afetam as propriedades da polpa assim como a cal, podendo substituí-la. Dosagens mais baixas não provocam coagulação ou não mantêm a polpa coagulada com a agitação, logo, são insuficientes. As mudanças provocadas pelos floculantes nas características da polpa não são satisfatórias, pois não minimizam a alta probabilidade de obstrução. Concluiu-se que é necessária a alteração do estado de agregação através do mecanismo de coagulação da polpa de minério de ferro a fim de se operar o sistema de maneira eficiente e com segurança.
Palavras-chave: Agregação/dispersão; Mineroduto; Reagentes alternativos da cal.

1 *Technical contribution to the 2nd International Symposium on Iron Ore, September 22 – 26, 2008, São Luís City – Maranhão State – Brazil*
2 *Chemical Engineer, MASc., Pipeline Operation Chief at Samarco Mineração S.A. – Mariana, MG, Brazil.*
3 *PHD, Professor Emeritus, Federal University of Minas Gerais – Belo Horizonte, MG, Brazil.*

1 INTRODUCTION

The most serious problems avoided in a long distance slurry pipeline upon shutdown are obstruction and compaction of the settled material. Under normal operation, some transport conditions and slurry characteristics, such as velocity, particle size distribution, solids concentration, etc., determine the probability of plug formation. The control of these variables guarantees the transport efficiency and safety. However, the system shutdown allows particle settling, which can result in obstruction by displacement of the material towards lower parts of inclined sections of the pipeline. In this case, the restart procedure represents a risk of pipeline rupture. Furthermore, excessive compaction of the sediment can make reslurrying impractical. When both conditions are present, the situation becomes significantly critical.

In order to avoid an unfavorable condition for restart, lime milk is added to the slurry transported by the pipeline. It modifies the iron ore slurry flow characteristics: it prevents the particles from sliding down the slopes leaving a thin layer of water on top of the solids bed so that the system can be reslurried and provides the benefit of keeping the sediment loose even after a long period of rest. On the one hand, lime addition is essential for an adequate shutdown and for a safe, effective restart of the system. On the other hand, the presence of calcium ions in the system causes scaling of important equipment, such as slurry storage tanks and process water piping, and degrades the filter media in the subsequent processing stage.

This study presents an evaluation of alternative reagents which were selected based on different aggregation mechanisms, taking into account their compatibility with the reagents added in the previous process stages, their effect on the subsequent process stages, the pipeline integrity (corrosion), environmental aspects and the final product quality. Two organic coagulants and two natural flocculants were tested: the quaternary ammonium salts polydiallyldimethylammonium chloride (PolyDADMAC) and epichlorohydrine-dimethylamine (Epi/DMA), tapioca starch and sodium carboxymethylcellulose (CMC), respectively.

The objective of this work is to propose an alternative to lime as a transport reagent for iron ore slurry pipelines. In order to achieve this objective, it was necessary to identify the mechanism responsible for generating the desired effect in the slurry flow behavior, i.e. minimize the probability of obstruction and reduce the sediment compaction upon shutdown of the system.

1.1 Aggregation and Dispersion

Most substances acquire a surface electric charge when brought into contact with a polar medium such as water and the electrical double layer model can be used to visualize the ionic environment in the vicinity of the charged particle. The internal layer, known as Stern layer, is composed of firmly attached counter-ions. In the external or diffuse layer the concentration of counter-ions decreases and that of co-ions increases with distance until a dynamic equilibrium with the solution is reached. The interactions between the van der Waals forces and the electrical forces are virtually additive. When it is assumed that only these two forces determine the stability level of the system then the DLVO theory applies. The DLVO theory explains the tendency of particles to either remain disperse or to aggregate. The net interaction can shift from attraction to repulsion and back to attraction with increasing distance between particles.(1,2)

Aggregation normally occurs by coagulation – double layer compression, charge neutralization or electrostatic patch – or flocculation.
For effective coagulation, the Coulombic energy barrier which causes repulsion should be lowered or completely removed so that the net interaction is always attractive. Double layer compression involves the addition of large quantities of indifferent electrolyte. Coagulation by this mechanism is not practical since it involves massive amounts of salt. It becomes efficient when highly charged counter-ions such as Fe^{+3} and Al^{+3} are added so as to lower the energy barrier by reducing the surface potential.(3)
When the charge density of an adsorbed polymer is higher than that of the particle surface, its uneven distribution will result in patches of positive and negative charges, which may interact resulting in attachment.(3)
Flocculation can be described in two main steps: (i) adsorption of a high molecular weight polymer in the particles surface and (ii) aggregate formation through bridging. Adsorption is normally attributed to electrostatic interaction or hydrogen bonds. The bridge mechanism assumes that the adsorbed polymer extends its loops and tails to the aqueous phase so that it collides with and attaches to another particle.(4)
The electrostatic stabilization is the dispersion mechanism described by the DLVO theory. It is based on an ionic repulsion between approaching particles that prevents attachment by means of a Coulombic energy barrier. Polymers can also stabilize dispersions by steric, electrosteric or depletion mechanisms. Steric stabilization occurs when two particles approach each other and the adsorbed polymer chains that extend into the dispersion begin to overlap and hinder the attachment of the particles. Electrosteric stabilization by ionic polymeric dispersants involves both electrostatic and steric mechanisms. Depletion stabilization results when a free nonadsorbed polymer generates repulsion and keeps the particles apart.(5)

2 MATERIALS AND METHODS

The iron ore sample tested in this work was obtained from the Alegria Complex in the state of Minas Gerais, Brazil. The run-of-mine ore was processed in pilot plant and laboratory according to the concentration process of Samarco Mineração S.A., which is based on reverse cationic flotation. The reagents used to produce an iron ore concentrate by removing the quartz impurity were amine (silica collector) and gelatinized starch (iron depressant). It was necessary to adjust the concentrate size distribution by grinding in order to meet the transport specification of 86-90% passing 325 mesh (44µm) and 3.5% maximum retained on 200# (74µm). Coagulant and nonionic flocculant (polyacrylamide) were added to the slurry as thickening aids, allowing the concentration increase to 70% solids by weight.
The primary slurry sample was characterized in terms of mineralogical and chemical content, specific surface area, specific weight and size distribution. It was then divided into four equal samples which were tested separately with the addition of four different reagents:
- Magnafloc 1697: Polydiallyldimethylammonium chloride supplied by Ciba Chemical Specialties in liquid form, density of 1.10g/cm^3, pH of 6.5, viscosity of 1160mPa.s (40%w/v, 25^{o}C); prepared at a concentration of 1%w/v;
- Magnafloc LT31: Epichlorohydrine-dimethylamine supplied by Ciba Chemical Specialties in liquid form, density of 1.10g/cm^3, pH of 5, viscosity of 975mPa.s (40%w/v, 25^{o}C); prepared at a concentration of 1%w/v;

- Tapioca starch supplied by HaloteK-Fadel in powder form, starch content of 75.3%, 99% passing 1mm, viscosity of 14mPa.s (2%w/v); prepared at a concentration of 2%w/v;
- Gabrosa 30C: Sodium carboxymethylcellulose supplied by Akzo Nobel in powder form, substitution degree of 0.75, viscosity of 800mPa.s (1%w/v, 25^{o}C); prepared at a concentration of 1%w/v.

Each reagent was tested at three different dosages – 5, 100 and 300ppm – and compared with both blank and reference samples. The latter was obtained by adding lime to the slurry to reach a pH of 11.6.

Fractions were taken from all samples in order to perform settling, rheology and penetration tests. The remaining part was agitated in separate vessels for a period of 24 hours. Rheology tests were performed during the first five hours and at the end of the agitation period settling, penetration and angle of repose tests were performed. The tests are described in the following topics.

2.1 Settling Test

The settling test was performed with the aid of 1000ml graduated cylinders. The level of settling solid/liquid interface was recorded at set intervals: 0, 15, 30, 45, 60 and 90 seconds and 2, 3, 4, 5, 10, 15, 20, 30, 45, 60, 90 and 120 minutes. The settling velocity was obtained from the data plot and at the end of the test the supernatant water was classified in terms of clarification: excellent (≈ 100NTU), good (≈ 600NTU), bad (≈ 1500NTU) and very bad (≈ 400.000NTU).

2.2 Rheology

A concentric-cylinder-type rheometer, Rheomat R-180, was used to measure shear stress at set shear rates, starting from 600/s and decreasing to the minimum shear rate for which it was possible to obtain accurate reading. The apparent viscosity was calculated at the lowest shear rate.

2.3 Penetration Test

The penetration test was performed in 600ml beakers where the slurry sample was allowed to settle for 24 hours. The penetrometer head was placed at the solid/liquid interface and weights were placed on the pan. The minimum weight for which the penetrometer head reached the bottom in one motion was recorded and checked against the reference value of 50g to provide an indication of compaction. Values bellow this reference indicate a “loose” bed of particles which is easy to reslurry. Figure 1 shows a picture of the counter-balance system used.[6]

Figure 1. Counter-balance system for the penetration test.

2.4 Angle of Repose Test

The angle of repose test was performed with the aid of a clear plastic tube, length 1200mm x diameter 63mm.[6] The tube was tilted to mix the slurry and then positioned at a 15% slope from horizontal on an inclined plane. The slurry was allowed to settle for 4 hours. Visual evaluation was made to determine whether there was plug formation and the parameters ***a*** and ***b*** were measured, as indicated in Figure 2. The plug indicates a high probability of pipeline obstruction and is characterized by ***b*** ≠ 0. The ideal situation in which the probability of obstruction is low corresponds to ***b*** = 0.

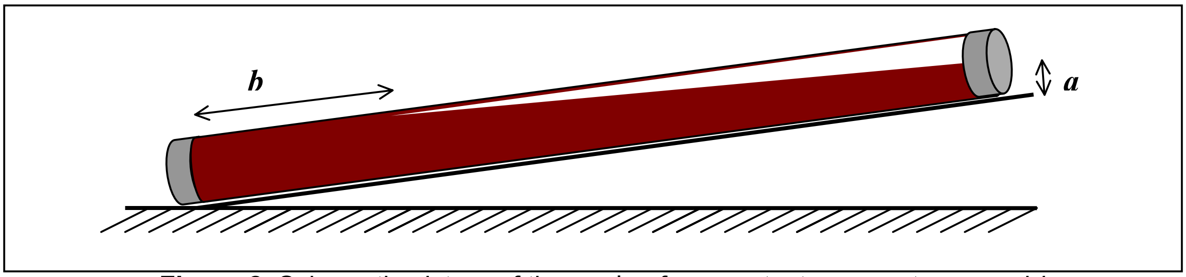

Figure 2. Schematic picture of the angle of repose test; parameters *a* and *b*.

3 RESULTS AND DISCUSSION

3.1 Concentrate Characterization

The concentrate sample produced in pilot plant and laboratory presented similar characteristics to those of the concentrate transported by the Samarco Pipeline. Tables 1 and 2 show the concentrate mineralogical and chemical compositions, respectively.

Table 1. Concentrate mineralogical composition, in % by weight.

Mineral	Specular hematite	Porous hematite	Goethite	Magnetite	Quartz
Average	39.9	42.4	15.2	2.0	0.6

Table 2. Concentrate chemical composition, in % by weight.

Component	Fe	SiO_2	Al_2O_3	P_2O_5	PPC	MnO_2	FeO
Average	66.85	1.56	0.28	0.043	2.39	0.07	0.69

The specific surface area obtained by the Blaine and the BET methods are presented in Table 3 along with the solids specific weight. The great difference in the specific surface area results was expected since the Blaine method provides an indirect indication based on permeability, unlike the BET method, which measures the effective area and takes into account the particles porosity.

Table 3. Concentrate specific surface area, in cm^2/g, and solids specific weight, in g/cm^3.

Parameter	Blaine	BET	Specific weight
Average	1,368	22,206	4.98

Size distribution analysis data is shown in Table 4. The pipeline specification for particle size was met: 86-90% passing 45μm, maximum of 3.5% retained on 75μm and maximum of 0.3 retained on 150μm.

Table 4. Concentrate size distribution data.

Parameter	-45μm (%)	+75μm (%)	+150μm (%)	D50 (μm)
Average	88.2	2.5	0.2	26

3.2 Settling Velocity and Supernatant Water Clarification

The settling test results are presented in Table 5 in terms of initial settling velocity and Table 6 shows the supernatant water classification.

Table 5. Settling velocity before agitation (BA) and after agitation (AA), in cm/s.

Test	Sample	Blank	5ppm	100ppm	300ppm	Reference
PolyDADMAC	1-BA	0.19	0.18	0.24	0.17	0.18
	1-AA	0.28	0.30	0.17	0.19	0.20
Epi/DMA	2-BA	0.12	0.12	0.24	0.17	0.19
	2-AA	0.34	0.34	0.18	0.21	0.24
Starch	3-BA	0.13	0.13	0.16	0.21	0.18
	3-AA	0.44	0.40	0.45	0.44	0.25
CMC	4-BA	0.14	0.13	0.06	0.03	0.16
	4-AA	0.47	0.46	0.44	0.28	0.24

Table 6. Supernatant water clarification before agitation (BA) and after agitation (AA).

Test	Sample	Blank	5ppm	100ppm	300ppm	Reference
PolyDADMAC	1-BA	--	--	++	+	++
	1-AA	--	--	-	++	++
Epi/DMA	2-BA	--	--	++	+	++
	2-AA	--	--	-	++	++
Starch	3-BA	--	--	--	-	++
	3-AA	--	--	--	--	++
CMC	4-BA	--	--	--	--	++
	4-AA	--	--	--	--	++

-- very bad; - bad; + good; ++ excellent

The blank sample presented an increase in settling velocity after agitation due to the adsorption kinetics of the flocculant used at the thickening stage. The adsorption equilibrium was achieved at the beginning of the agitation period, thus enhancing the flocculation efficiency. The increase can be also related to the polymer configuration. At rest, each macromolecule can be found in the state of the lowest level of energy consumption, in the shape of a three-dimensional coil. During the shear process, the molecules are more or less oriented in the shear direction, disentangled to a certain extent or even completely disentangled. It is reasonable to admit that the polymer chains are broken and that the slurry ageing leads to dispersion,(7) which would result in settling velocity decrease. However, this effect did not become apparent, since the effect of adsorption equilibrium and polymer configuration was predominant.

The results obtained with addition of 5ppm of the reagents were very close to the ones obtained for the blank sample. Different behaviors were observed as the dosage increased, though.

The addition of 100ppm of PolyDADMAC or Epi/DMA allowed the particles coagulation so that the settling velocity increased to 0.24cm/s before agitation. The highest dosage (300ppm) was excessive, which was evident by the decrease in settling velocity. After the agitation period, the system which was initially coagulated was dispersed and the system which had excessive positive charge was neutralized with agitation, due to the ageing of the slurry. The supernatant water clarification results confirm this finding: for 100ppm the turbidity increased and for 300ppm it decreased after agitation.

The results for lime addition (reference sample) and addition of 300ppm of PolyDADMAC or Epi/DMA did not change significantly with agitation. However, the settling velocity was much lower than that of the blank sample after agitation. Regarding the organic coagulants, this effect can be assigned to competitive adsorption with the thickening flocculant. They can adsorb much faster due to their smaller size and the electrostatic attractive force. Furthermore, their concentration was much higher. However, when it comes to increasing settling velocity, coagulants are known to be ineffective.

The supernatant water classification confirms the coagulation of the systems containing the highest dosages of lime or organic coagulants: it was initially good or excellent and excellent after agitation.

The settling velocity increased with increasing dosages of starch before agitation; after agitation it reached values as high as for the blank samples. The starch adsorption equilibrium achieved with agitation and the new polymer configuration provided the best conditions for flocculation; chain breakage and ageing did not become apparent.

It was possible to observe the effect of dispersion by steric stabilization or by depletion in the samples containing CMC since the settling velocity became extremely low with increasing dosages. The high viscosity of the aqueous phase must have influenced the results as well. On the other hand, the CMC long chains are highly susceptible to breakage in the presence of shear. The steric hindrance is lower in this case and improves the bridge formation process, thus increasing the settling velocity. Nonetheless, the sample which received the highest dosage of CMC still presented lower settling velocity than the blank sample.

3.2 Rheological Behavior

In order to compare the rheology test results, the apparent viscosity was calculated at 350/s, 30°C. This shear rate was the lowest obtained using the Rheomat R180 and represented the lowest possibility of turbulent regime. Table 7 presents the results before agitation and after 3 hours of agitation (DA). After a longer time submitted to shear, the samples viscosity decreased significantly and it was not possible to perform the rheology tests without error.

Table 7. Apparent viscosity before agitation (BA) and after 3 hours of agitation (AA), in mPa.s.

Test	Sample	Blank	5ppm	100ppm	300ppm	Reference
PolyDADMAC	1-BA	16.6	16.5	18.0	13.8	15.3
	1-AA	*	11.3	12.4	12.8	13.9
Epi/DMA	2-BA	11.6	12.0	14.4	13.4	15.1
	2-AA	*	*	11.6	12.3	13.0
Starch	3-BA	14.7	14.1	15.5	17.7	15.5
	3-AA	*	*	*	*	11.9
CMC	4-BA	13.6	14.1	18.7	29.0	16.3
	4-AA	*	*	*	16.5	13.6

The thixotropy phenomenon was observed for all samples since the apparent viscosity decreased with time. The asterisk represents the situations of remarkable viscosity reduction before 3 hours of agitation. The blank sample results show the effect of slurry ageing as well as polyacrylamide configuration change and adsorption kinetics, as mentioned before. Upon addition to the slurry, the adsorbate concentration reaches the maximum level in the aqueous phase but decreases gradually with time until the equilibrium state is reached. As the flocculant is transferred to the solids surface, a decrease in flow resistance is expected. No significant difference was verified with addition of 5ppm of the reagents tested.
The rheological behavior of the samples coagulated with lime, 100 and 300ppm of the organic coagulants changed with agitation due to ageing. At higher dosages of the reagents, it can be inferred that the concentration in the aqueous phase of the polyacrylamide added previously at the thickening stage was higher due to preferential adsorption of the coagulants, thus keeping the viscosity higher as well.
The apparent viscosity of the samples containing starch increased with increasing dosages, as expected. However, agitation allowed the reagent to transfer to the solids surface and the chains disentanglement, resulting in lower flow resistance. The CMC test results were similar to those with starch, although it presented much higher initial viscosity values for addition of 100 and 300ppm of the reagent. This was expected since the CMC chains are significantly longer than the starch chains. For both reagents, viscosity decreased with agitation as the chains were broken.
The rheology test results were consistent with the settling test results.

3.3 Sediment Compaction

The penetration test results are shown in Table 8. Except for the sample with 300ppm of CMC, all results were acceptable. The compaction exceeded the reference value of 50g in some cases but it is reasonable to tolerate a 10g deviation, considering the methodology imprecision. It is worth mentioning that the compaction was either kept low or suffered considerable reduction after the agitation period, except for the highest dosage of CMC.

Table 8. Compaction in terms of minimum penetration weight before agitation (BA) and after agitation (AA), in g.

Test	Sample	Blank	5ppm	100ppm	300ppm	Reference
PolyDADMAC	1-BA	55	45	45	50	35
	1-AA	20	20	20	20	20
Epi/DMA	2-BA	45	35	35	35	25
	2-AA	20	20	20	20	20
Starch	3-BA	55	55	60	50	30
	3-AA	40	30	40	45	25
CMC	4-BA	60	60	60	80	40
	4-AA	20	30	50	90	20

3.3 Probability of Plug Formation

The parameters ***a*** and ***b*** measured in the angle of repose test are presented in Table 9.

Table 9. *a* and *b* values measured in the angle of repose tests, in cm.

Test	Sample	Blank	5ppm	100ppm	300ppm	Reference
PolyDADMAC	***a***	1.4	1.5	1.5	2.0	2.1
	b	32	28	22	0	0
Epi/DMA	***a***	1.3	1.5	1.6	1.4	1.8
	b	34	39	16	0	0
Starch	***a***	1.2	1.3	1.1	1.7	1.7
	b	37	39	26	43	0
CMC	***a***	1.2	1.3	1.1	0.8	2.1
	b	34	37	40	40	0

Generally, ***a*** is higher when ***b*** = 0, but one parameter is independent from the other. Most samples presented plug formation in the angle of repose test. The only ones indicating a low probability of pipeline obstruction were the reference sample and the samples with addition of 300ppm of the organic coagulants. Supernatant water clarification data obtained from the settling test indicated that these samples were effectively coagulated.

3.4 Final Considerations

From the point of view of fluid mechanics applied to transport of homogeneous systems such as iron ore slurry, one should distinguish between carrier fluid (usually water) and transport fluid. The latter is composed by the liquid phase and by the finest solids fraction forming a homogeneous system. The remaining particles, which are easily separated from the liquid, are carried by the transport fluid. The coagulation allows the transfer of particles from the fluid phase to the solid phase so that the transport fluid becomes more water-like.

It is important to bring up that the iron ore concentrates with high content of specular hematite and low content of goethite obtained from Germano and Fazendão mines do not form plugs in the angle of repose test, even without addition of transport reagents. Iron ore from Germano was processed for many years in Samarco and there is no record of pipeline obstruction during this period, except in one event when the particle size was completely out of specification. Concentrates like the ones mentioned do not generate a significant amount of fines in the grinding stage due to its low goethite content and, upon settling of the solids, the supernatant water presents almost no turbidity. The material studied in this work contained low content of specular hematite and high content of goethite, so the probability of plug formation had to be decreased by the coagulation mechanism.

4 CONCLUSIONS

The addition of 300ppm of polyDADMAC or EpiDMA or the addition of lime to pH 11.6 allows the best supernatant water clarification in the settling test, both before and after agitation. This effect was assigned to coagulation of the ultrafine and colloidal particles. Lower dosages of the coagulants or addition of the flocculants (starch and CMC) do not provide surface charge neutralization, thus resulting in bad or very bad clarification.

Since coagulation is the mechanism responsible for minimizing the probability of plug formation upon pipeline shutdown, lime can be replaced by 300ppm of PolyDADMAC or Epi/DMA. Addition of the flocculants does not provide the necessary change to the slurry characteristics so that replacement with starch or CMC is not recommended.

REFERENCES

1 RAVINA, L. Everything you want to know about coagulation and flocculation, 4ª Ed., 1993. Available at: <http://www.mtec.or.th/labs/powder/book/coagulation.pdf> Access in: 10 jun, 2008.

2 SHAW, D. J. **Introduction to colloid and surface chemistry** (Colloid and Surface Engineering). 4ª ed. Oxford: Butterworth-Heinemann, 1992.

3 KIM, Y. H. **Coagulants and flocculants**; theory and practice, 1ª Ed. Littleton: Tall Oaks Publishing, Inc., 1995.

4 KITCHENER, J. A. Principles of action of polymeric flocculants. **British Polymer Journal,** vol. 4, pp.217-229, 1972.

5 KISSA, E. **Dispersions;** characterization, testing and measurement. 1ª Ed. New York: Marcel Dekker, Inc., 1999. (Surfactant Science Series, vol. 84).

6 PIPELINE SYSTEMS INC., **Laboratory tests procedures** (60-G-M-06), 1997.

7 SAMPAIO, D. A. Estudo das propriedades de concentrados de minério de ferro da Samarco Mineração S. A. e sua influência no potencial de entupimento do mineroduto. Belo Horizonte: Escola de Engenharia da Universidade Federal de Minas Gerais, 2002 (Masters Dissertation).