

Evaluation of the Performance of a Local Acid Activated Clay on the Decontamination of Solvent Extraction Plant Organic

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Abstract

Imported acid activated bentonite clay is used in many solvent extraction (SX) plants of the Democratic Republic of Congo (DRC) to decontaminate the organic phase.

This paper reports on test works carried out to evaluate whether clay sourced and activated locally could be used for the decontamination of oxime-based DRC SX plant organics. The sample of clay used was collected on the bank of Kalubwe River in Lubumbashi. The pre-treatment included: drying and screening (100 % passing 212 μm), activation in 10%, 20% and 30% sulfuric acid respectively during 30 min, 45 min and 60 minutes for each acid concentration, drying and further grinding. Organic performance parameters tested included Phase Disengagement Time, Extraction and Stripping Kinetics, copper selectivity over iron, and the loss of healthy oxime subsequent to the clay treatment process.

- Regarding the phase disengagement time, the higher the concentration of the leaching acid, and the longer the leaching time, the closer the performance of the local clay was to the imported clay. The same applies regarding extraction and stripping kinetics, with an optimum clay dose of 1 g activated clay per litre of plant organic.

- Although the behaviour was relatively similar, lower acid activation time of local clay seemed to favour copper selectivity over iron.

- The longer the activation time and the higher the acid concentration, the lower the loss of healthy oxime during the clay treatment. The higher the clay dose used, the higher the amount of healthy oxime lost.

Key words: Solvent extraction, phase disengagement time, extraction and stripping kinetics.

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I. Introduction

In 2014, Cu production of the Democratic Republic of Congo crossed the Milestone of one million tonnes per annum, of which more than 70% were produced as cathodes via the process of leaching, solvent extraction and electrowinning (Division Provinciale des Mines, 2014; Matthew Hill, 2014; Michael, 2014; Mining Weekly, 2014 a, 2014 b). At that time, not less than twenty solvent extraction plants (small, medium and big size) were within production phase in what was Katanga Province. Many projects were within development or expansion phase.

The purification of a copper leach solution by solvent extraction involves the use of an organic phase containing an oxime based extractant dissolved in a diluent. Over time, variable quantities of contaminants can build up in the organic phase. Contaminants can be natural animal or vegetal organic compounds contained in the ore leached or chemicals or products of chemical reactions occurring upstream or downstream of the solvent extraction step, or products of slow or fast degradation products of the components of the organic phase (BASF Mining and oilfields chemicals, 2011; Dudley et al, 2006; Miller, Readett and Hutchinson, 1997; Virnig, Mattison, and Hein, 2002, 2003, 2004). Depending on working conditions and on the chemicals involved, degradation mechanisms of the plant organic may include acid catalysed hydrolysis, oxidation etc. The presence of contaminants in a plant organic can significantly affect its physical proprieties, and therefore the behaviour of a solvent extraction plant (BASF Mining Solutions, 2013; Cognis BASF, 2007).

The decontamination of an oxime based organic has been discussed in many papers (Jenkins, 1991; Dombrowski, Henderson, 1997; Dudley et al, 2006; Mattison, Kordosky and Champion of Henkel Corp, 1983). It is carried out by mixing it with activated bentonite clay. Contaminants will be preferentially adsorbed onto the large active surface of the clay. The large active surface of the clay is created during its preparation which includes fine grinding and acid leaching. To be efficient, the process of the production of the clay must include

an activation step. The activation of a clay has been described exhaustively (Al-Zahrani, Al-Shabrani and Al-Tawil, 2000; Seghairi and Achour, 2003; Seghairi, Koussa and Achour, 2004). It may consist on a simple calcination (500 – 700 °C), or a leaching with inorganic acids, or a combination of both calcination and leaching. The acid leaching of the rough clay is followed by filtration, washing with distilled water, and drying. Subsequently to the calcination, the evaporation of water yields a porous structure offering a large reaction area. The acid leaching of clays changes their structure, creating new pores and increasing thus their superficial acidity following the replacement of some cations such as Al^{3+} , Fe^{3+} and Ca^{2+} by H^+ (Al-Zahrani, Al-Shabrani and Al-Tawil, 2000; BASF Mining Solutions, 2013; Bishop et al, 1999; Dombrowski and Henderson, 1997).

The average consumption of clay for the decontamination of a plant organic depend on typical plant conditions, including its composition, and its level of contamination. In many DRC plants, consumption ratios from 2 to 30 kg of clay per cubic metre of plant organic are reported. Considering only relatively big size plants, and according to our own estimation, the market of activated clay in the DRC could exceed 15 tons per month, expected to grow with the copper SX business.

All DRC SX operations where clay treatment is practiced are currently using imported activated bentonite clay for the decontamination of their plant organic. If transport cost and import taxes are added to the production cost of the imported clay, it can be expected that activated bentonite clay produced locally could compete with imported clay. The main objective of this study is to evaluate the performance of a clay sourced and activated locally for the decontamination of a plant organic. The study included two steps: The first was carried out in 2012 with a plant organic which was received being already contaminated (Twite and Kongolo, 2012). At that time, the only parameter used to evaluate the performance of the local clay prepared in the lab was the measurement of phase disengagements after mixing organic samples decontaminated with various lots of the local clay made up in the lab in various conditions with samples of aqueous taken from a big volume of a copper leach solution. The second was carried out in 2014 using a plant organic which “as received” was relatively healthy. It has been “artificially” contaminated in the lab by oxidation with potassium permanganate (Kanyembo and Tshibanda, 2014). This paper reports mainly on the results of the second part of study, although the results of the first part were used in the second phase. The performance of the local clay was compared to an imported clay.

II. Methodology

The sample of rough clay that was used in this study was taken at random on the bench of Kalubwe river within the residential area of Lubumbashi Town. The sample was subject to a physical pre-treatment including the following steps: mixing, drying, grinding and sizing at 100% passing 212 μm (Kanyembo and Tshibanda, 2014; Twite and Kongolo, 2012). The rough and non-exhaustive analysis has revealed mainly the following components: SiO_2 : 56.9%; Al_2O_3 : 1.2%; Na_2O : 1.0%; Fe_2O_3 : 0.9%; MgO : 0.9%; CaO : 0.3%; K_2O : 0.3%. The rough specific gravity was 2.32 kg/dm^3 (Twite and Kongolo, 2012).

The activation of the so pre-treated clay sample was carried out by mixing in sulfuric acid. Three acid concentrations were used (10%, 20% and 30%). Three leaching times have been chosen: 30, 45 et 60 minutes. The temperature was in each case maintained at 100°C. The combination of these activation treatments has yield 9 lots of activated clay which have been used for decontamination tests of the organic collected from the SX plant of Ruashi Mining (Kanyembo and Tshibanda, 2014). As collected from the SX plant, the organic was relatively healthy, with no significant contamination as measured by phase disengagement tests. We have managed to provoke the contamination in the lab by contacting the healthy organic with a strong oxidant. The non-contaminated organic from the SX plant was mixed during 10 minutes with a 2N potassium permanganate solution ($KMnO_4$) at a 5/1 volumetric organic / aqueous ratio, followed by filtration on IPS phase separator paper. In practice, permanganate anion can be formed in some conditions in electrowinning cells when the electrolyte contains manganese ion. The ratio of 5/1 has been selected to avoid excessive oxidation of the plant organic.

The equipment and the procedure which have been used for the quality control of the organic phase were as per BASF standard tests of quality control for solvent extraction reagents (Redbook Mining Solutions BASF, 2014). Generally, when compared with a healthy organic phase, the properties of a contaminated organic phase can be variably affected. These were evaluated for the plant organic before and after decontamination with clay. The performance of the locally activated clay for the decontamination of the plant organic has been compared with the non-activated local clay on one end, and with an imported clay on the other hand. The parameters used for the evaluation of the reactivity of the clay samples have been variably affected depending on the concentration of the sulfuric acid used for leaching, as well as the length of the activation process.

The various lots of clay activated in the conditions described above have been used for the decontamination of the plant organic. This organic purposely contaminated in the laboratory has been treated with increasing doses of clay from the various lots prepared in the lab. The performance of clay samples from

various lots has been evaluated by measuring a few characteristics of the organic after the decontamination including:

- *The phase disengagement time:* It is the time taken by the organic phase to separate with the aqueous phase (in this case the leach solution) after having been mixed in organic continuity. An emulsion of organic and aqueous is said to be organic continuous if it is made of aqueous droplets dispersed in an organic continuum. When the phase disengagement after mixing in organic continuous is significantly over 120 seconds, it is likely that the organic phase involved contains contaminants which inhibit the coalescing of aqueous droplets (Redbook Mining Solutions BASF, 2014).
- *Extraction kinetics:* According to BASF quality control tests standards, extraction kinetics is the ratio between the copper extracted after 30 seconds of mixing of the organic and the aqueous phases, and what is extracted at the equilibrium (The equilibrium is assumed in the lab after 300 seconds of mixing) (Redbook Mining Solutions BASF, 2014).
- *Stripping Kinetics:* It is defined the same way as extraction kinetics, but relative to the copper that has been stripped.
- *Copper selectivity over iron:* it is the ratio of the quantities of the two cations which have been effectively transferred over the solvent extraction process which includes extraction and stripping (Cognis BASF, 2007). Among all ions contained in DRC leach solutions from copper ores, only Fe^{3+} can load onto oximes in certain conditions (Cognis BASF, 2007). Manganese can only be physically transferred from the leach solution to the electrolyte via aqueous entrainment in the loaded organic.
- *The loss of non-contaminated oxime* subsequent to the decontamination with activated clay: it is the difference between the oxime concentration of the organic before and after clay treatment. The oxime molecule being polar, a variable amount of uncontaminated oxime can be lost by absorption onto the clay used to decontaminate the organic (Bishop et al, 1999; Kabobo et al, 2013; Keith et al, 2011a, 2011b; Virnig, 2013). The quantity of oxime lost depends on the dose, the treatment time, and most likely on the type of clay (Kabobo et al, 2013).

III. Results and discussion

III.1. Phase disengagement tests

Figures 1, 2 and 3 show trends of phase disengagement time (PDT) versus the dose of clay activated locally at various concentrations of sulfuric acid during 30, 45 and 60 minutes respectively.

Comment from figures 1, 2 and 3 is:

- The performance of untreated clay is relatively poor. When non activated clay is used to decontaminate a plant organic, a minor improvement of PDT is observed, but the separation time does not decrease below 120 seconds.
- The increase of acid concentration from 10 to 30 % allows an increase of the reactivity of untreated clay, in terms of achievable PDT after clay treatment (figures 1 and 2).
- On the other hand, the increase of the activation time improves its ability to decontaminate an organic, especially when the acid concentration is in the range of 20 to 30% (figures 1 and 2)
- Within the parameters used for the activation of the rough clay, the performance of the imported clay in terms of its capacity to improve phase disengagement is nonetheless slightly higher than that of the local clay. It is highly likely that the finer grain size of the imported clay favours its reactivity to the disadvantage of the locally prepared clay. (The grain size of the locally prepared clay could be a good parameter to optimise regarding its impact on the PDT, etc in future tests).
- Plots of PDT versus the clay dose flatten from a dose of 1 g and above per litre of the treated organic. This clay dose allows a reduction of PDT below 120 seconds. In this special case, the clay dose of 1 g/L can be taken as optimal.

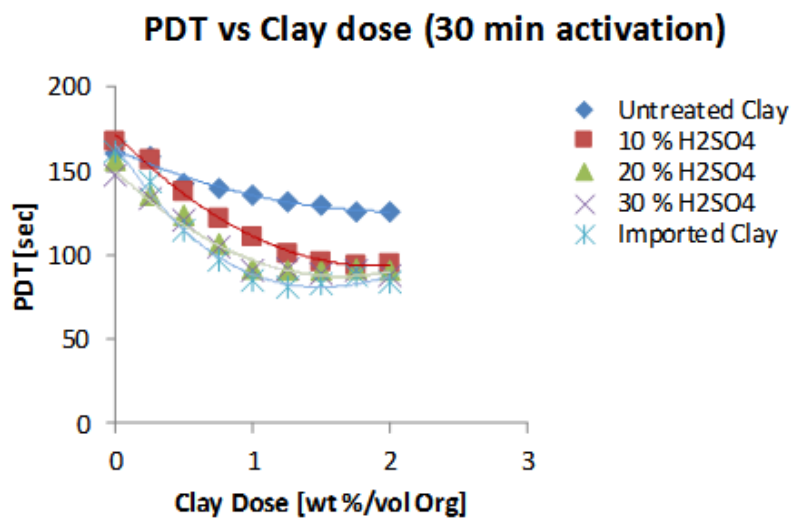


Figure 1. Phases Disengagement Time (PDT) versus the dose of clay activated at various acid concentrations during 30min

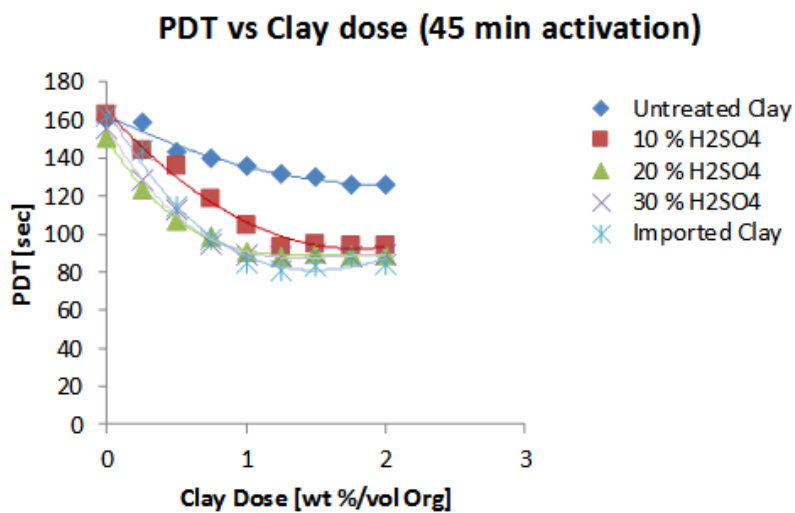


Figure 2. Phases Disengagement Time (PDT) versus the dose of clay activated at various acid concentrations during 45 min

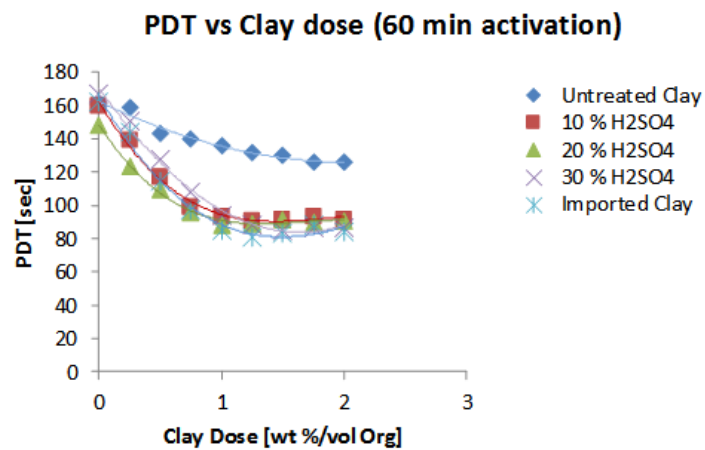


Figure 3. Phases Disengagement Time (PDT) versus the dose of clay activated at various acid concentrations during 60 min

III.2. Extraction kinetics

Figures 4, 5 and 6 give trends of extraction kinetics versus the dose of the clay activated locally with various concentrations of sulfuric acid during 30, 45 and 60 minutes respectively.

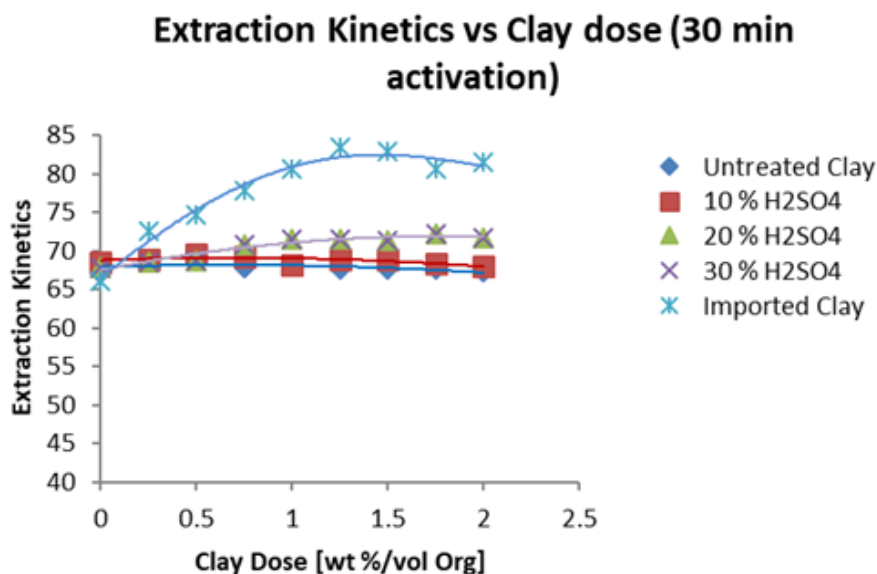


Figure 4. Extraction kinetics versus dose of clay activated at various acid concentrations for 30min

The examination of figures 4, 5 and 6 leads to the following comment:

- In the range of optimisation parameters selected for the activation treatment of the local clay, the increase of activation time allows an increase of its ability to improve extraction kinetics of the plant organic (figure 4).
- From a clay dose of 1 g/l used for the decontamination of the organic, almost all extraction kinetics curves start flattening. In line with the improvement of extraction kinetics, this dose could be thus taken as optimal.
- The higher the acid concentration during the activation treatment of the rough clay, the higher reactivity it will have, especially when the activation is relatively long, and the best the capacity of that clay to restore the extraction kinetics of a plant organic during the decontamination process. Considering these results, it may be possible to further improve the reactivity of the local clay vis-à-vis its extraction kinetics by increasing the acidity beyond 30% and/or the activation time beyond 60 min. This is because the treatment process of the rough clay leads to an increase of its specific area, and thus the number of active sites (Dudley et al, 2006).
- Rough local clay (nonactivated) is virtually ineffective. Its curves are quasi horizontal.

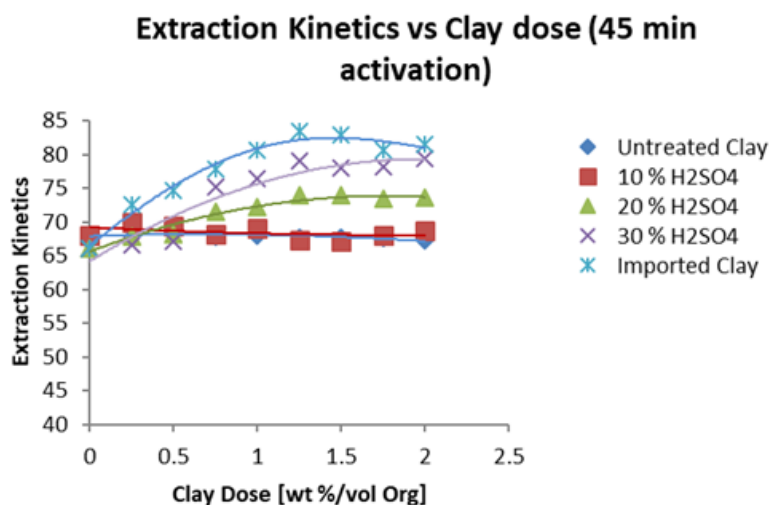


Figure 5. Extraction kinetics versus dose of clay activated at various acid concentrations for 45min

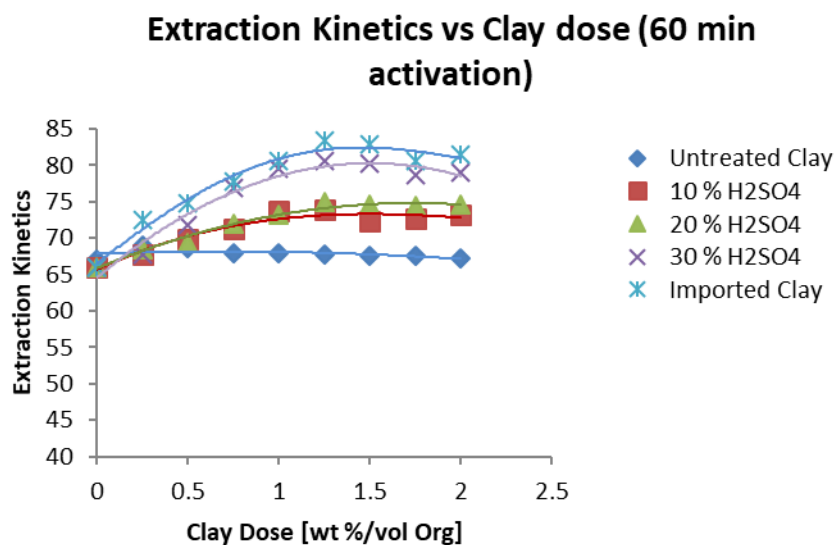


Figure 6. Extraction kinetics versus dose of clay activated at various acid concentrations for 30min 60min

III.3. Stripping Kinetics

Figures 7, 8 and 9 give trends of stripping kinetics versus local clay dose activated at various sulphuric acid concentrations for 30, 45 et 60 minutes respectively.

Apart from a few differences, from the examination of figures 7, 8 and 9, the comment made above for extraction kinetics applies for stripping kinetics:

- The performance of the clay is improved with the increase of activation time and the acid concentration. (Figure 4).
- Regarding stripping kinetics, a clay dose of 1 g/l could be taken as optimal to decontaminate the plant organic used in the tests.

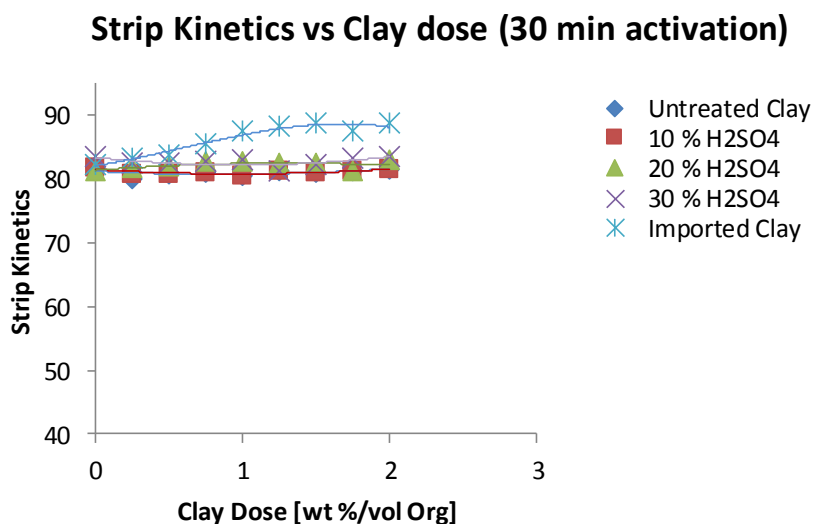


Figure 7. Stripping kinetics versus dose of clay activated at various acid concentrations for 30min

- The effect of imported clay differentiates itself from the activated local clay within the range of acid concentration and activation time used during our tests.
- Rough local clay (nonactivated) is virtually ineffective. Its curves are quasi horizontal.

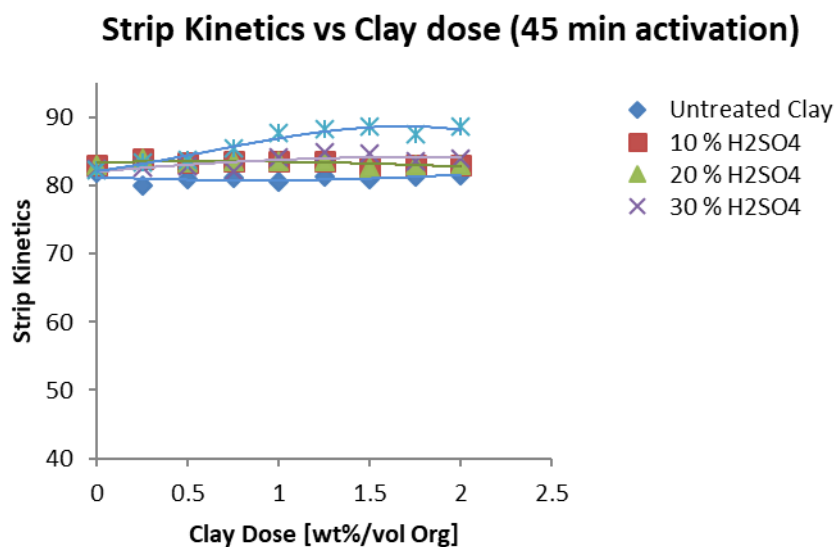


Figure 8. Stripping kinetics versus dose of clay activated at various acid concentrations for 30min 45min

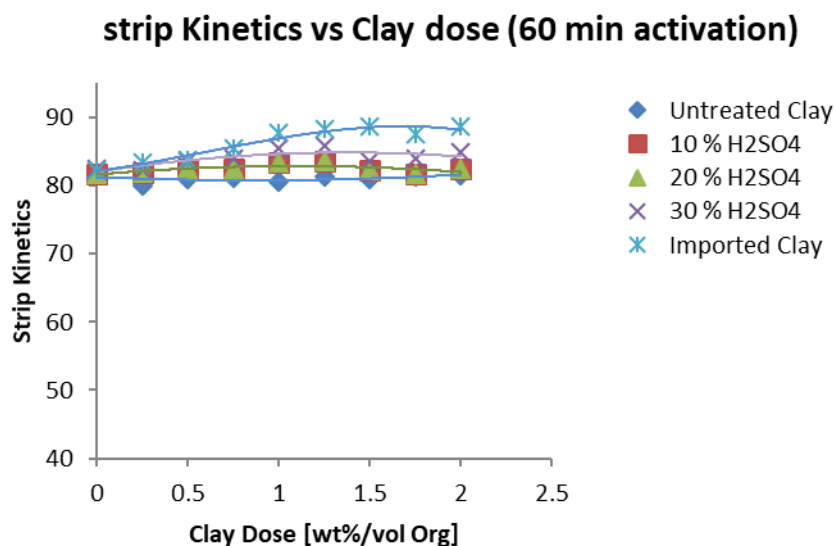


Figure 9. Stripping kinetics versus dose of clay activated at various acid concentrations for 30min 60min

III.4. Cu/Fe Selectivity

Figures 10, 11 and 12 show trends of Cu/Fe selectivity relative to the dose of local clay activated with various sulfuric acid concentrations for 30, 45 and 60 minutes respectively.

The following comment can be made from the observation of figures 10, 11 and 12:

- In virtually all scenarios, Cu/Fe selectivity has increased significantly from a dose of 2 g/l of organic onward. It could be interesting to check with further tests whether there could be additional benefits on the selectivity if the dose is increased above 2 g/l. However, it is important to note that this could be to the detriment of the oximes content of the organic as shown below on section discussing the loss of healthy organic during clay treatment.
- A lengthy activation is somehow detrimental to the Cu/Fe selectivity.

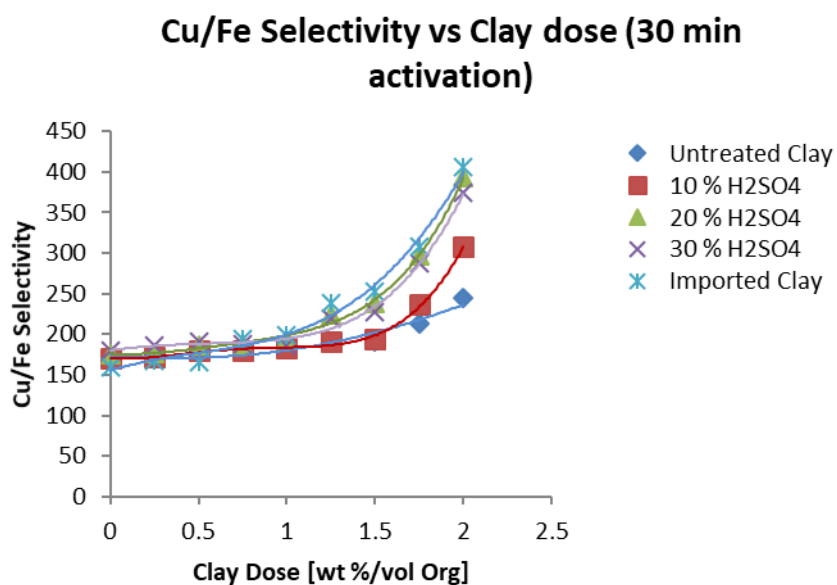


Figure 10. Copper selectivity over iron versus dose of clay activated at various acid concentrations for 30min

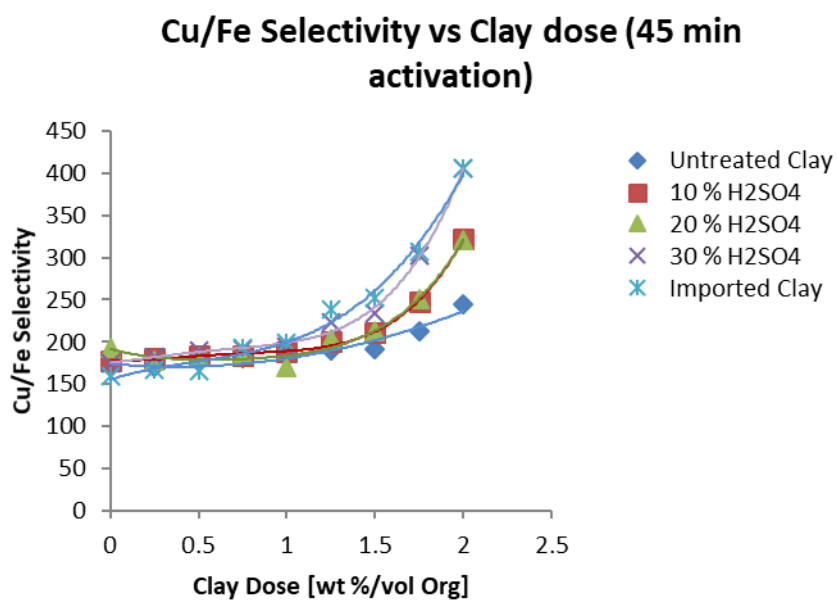


Figure 11. Copper selectivity over iron versus dose of clay activated at various acid concentrations for 45min

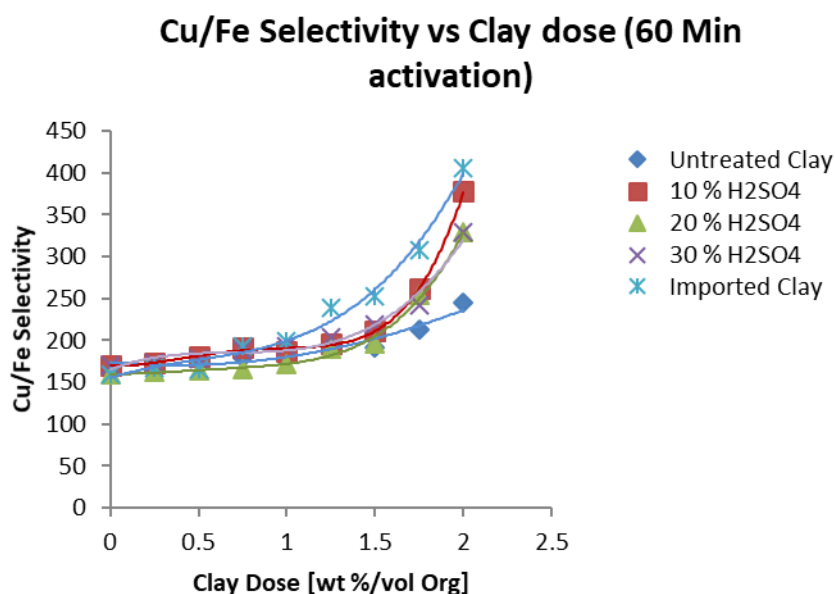


Figure 12. Copper selectivity over iron versus dose of clay activated at various acid concentrations for 60min

III.5. Loss of healthy oxime

Figures 13, 14 and 15 give trends of the loss of healthy oxime relative to the dose local activated clay at various concentrations of sulfuric acids for 30, 45 and 60 minutes respectively.

The following comment could be made based on figures 13, 14 and 15:

- During a normal clay treatment process a loss of a healthy portion of the oxime is almost unavoidable. The magnitude of the loss varies closely with the dose of the clay from 0.5 g/l onward, especially if the clay used has been activated with a relatively low acid concentration for a relatively short period (Figures 14 and 15). Compared to the local clay, the imported clay caused a lower loss of healthy oxime.
- At least 60 min of activation of the local clay, at a sulfuric acid concentration of at least 20% to have the loss of healthy oxime to be in the same range as the imported clay. The performance of local clay is thus favoured by an increase of both the activation time and the concentration of sulfuric acid during the activation process.

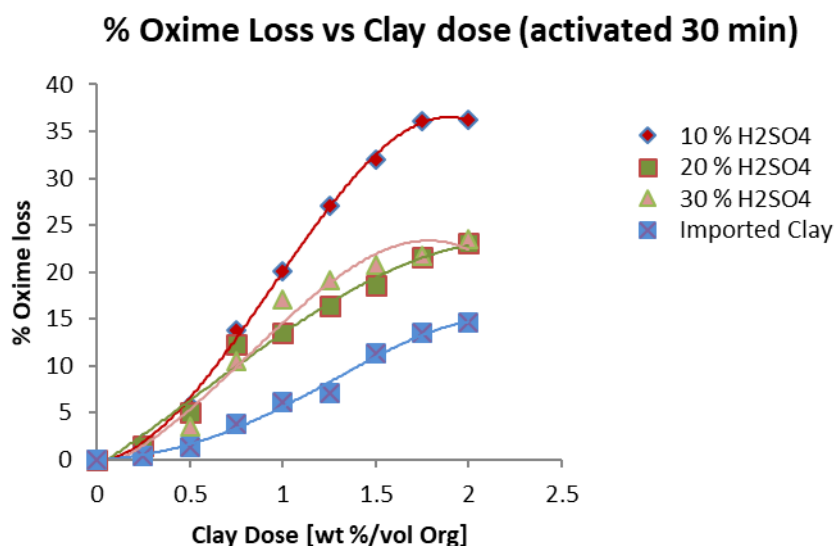


Figure 13. % of oxime lost versus dose of clay activated at various acid concentrations for 30min

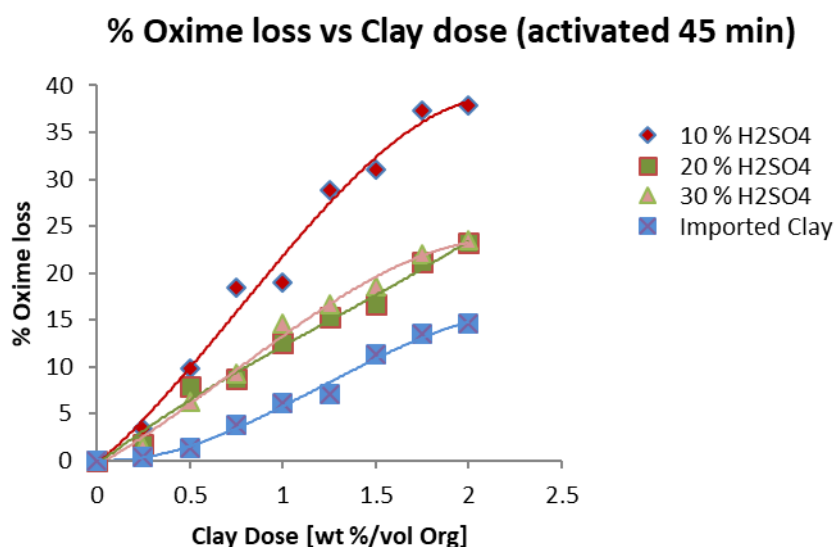


Figure 14. % of oxime lost versus dose of clay activated at various acid concentrations for 45min

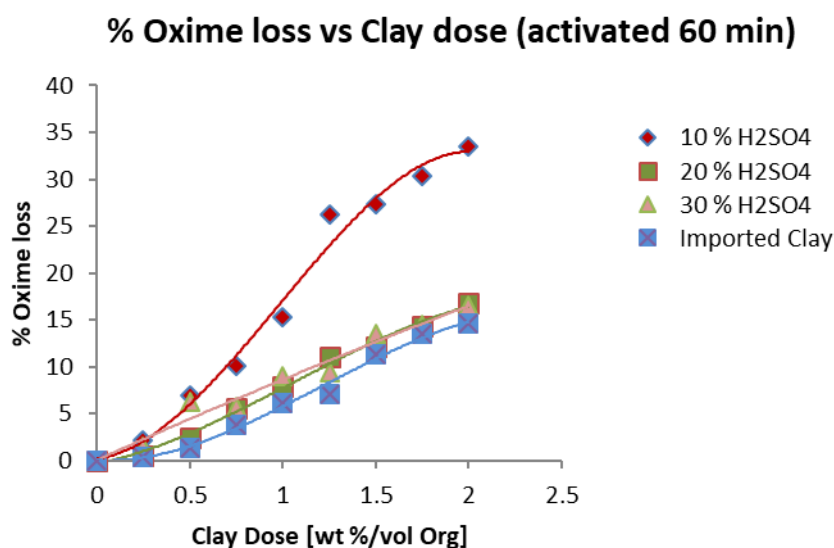


Figure 15. % of oxime lost versus dose of clay activated at various acid concentrations for 60min

IV. Conclusion

The results show that it is possible to optimise the activation treatment of a local clay to confer it properties close to those of good quality imported clay.

Within the range of the parameters in the tests, the longer the activation of the local clay (60 minutes), and the higher the acid concentration (30 % H₂SO₄), the better the reactivity for the improvement of phase separation time, extraction and stripping kinetics. The limiting factor in terms of activation parameters recommended seems to be the copper selectivity over iron which tends to decrease with the aggressivity of the activation. The optimal clay dose in the case of the organic used during our tests was 1 g of activated clay per litre of contaminated organic. There are grounds for more aggressive and longer activation tests of the local clay than those selected for the current study. But the impact of those conditions on copper selectivity over iron will need to be clarified.

The current study has shown that a local clay activated in specific conditions is suitable for the decontamination of a plant organic. The current study can be supplemented with a deeper evaluation of geological aspects of the site the rough clay sample has been taken from. On the other hand, as Kalubwe site is within a residential area, it is recommended to check whether the current results can be applicable to a representative sample of clay taken from a remote site where the operation of a mine would not prejudice the

rights of residents. Finally, a more exhaustive chemical analysis of Kalubwe clay could be beneficial. The impact of grain size could also be more deeply investigated.

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