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Removal of Arsenic from Wet Scrubbing Wastewater

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Abstract

Arsenic removal is hindered by its valence state. Addition of lime into wastewater containing arsenic gives benefits through the formation of low-soluble calcium arsenate, but the mechanism involved in the reduction of arsenic dissolution is not well known yet. Hence, in the present work different Ca/As ratios from 0 to 70% w/w were tested with the aim of finding the best conditions for removal of As from water (neutral tests) or solution (acid tests) containing sulphate ions. These solutions simulated aqueous streams coming from a wet scrubber for treatment of flue gas. Moreover, 5 g L^{-1} of iron chloride were tested as additive in the acid tests.

In the optimum operating conditions, nearly 99% precipitation yield was obtained for both As(III) and As(V) in less than 1 h; the optimum process conditions were 10 g L^{-1} of CaO without $FeCl_3$ for As(III) and 9 g L^{-1} of CaO and 5 g $^{-1}$ $FeCl_3$ for As(V) in acid solutions. As regards neutral solutions, 1 g L^{-1} of CaO is enough to precipitate around 99% of As(III) whereas the same result for As(V) is achieved by a higher CaO concentration (40 g L^{-1}). Iron chloride had a negative effect on As(III) precipitation.

Keywords: Arsenic; Flue gas; Scrubbing; Lime; Precipitation

1. Introduction

Arsenic contamination causes severe health problems around the world. Arsenic has found widespread use in agriculture and industry. Most of these activities have been broken off, but residues and the generation of arsenic wastes from smelting of various ores produce environmental pollution. Arsenic can be found in waste streams from a variety of industrial processes. For example, arsenic wastes are generated from petroleum refining, glass melting, and the smelting of ores that are mined for their lead, copper, zinc, gold and silver contents. Arsenic is also released into the environment by the dispersion of arsenic-containing fertilizers, pesticides and wood preservatives (Bothe and Brown, 1999). Some methods for removal of arsenic from various industrial effluents have been studied and proposed. Arsenic can not be destroyed but only converted into different forms or transformed into insoluble or stable compounds in combination with other elements, such as iron. Arsenic wastes may contain many impurities such as lead, iron and selenium. These elements can often be expensive to remove and arsenic is stockpiled as waste. However, arsenic with a purity greater than 95% may economically be recovered for manufacture of arsenical wood preservative, chromates copper arsenate (CCA) and ammoniacal copper-zinc arsenate (ACZA). The largest end use for arsenic trioxide is in production of wood preservatives (Reese, 2016). High purity arsenic metal (≥99.99%) is used in manufacture of crystalline gallium arsenide, a semi-conductive material used in optoelectronic circuitry, high speed computers and other electronic devices.

Arsenic can be removed from contaminated water by both physico-chemical and biological methods. These are classified below:

(I) physico-chemical techniques:

    (a) adsorption;

    (b) ion exchange;

    (c) precipitation–coagulation;

    (d) membrane filtration;

    (e) permeable reactive methods.

(II) Biological techniques:

    (a) phytoremediation;

    (b) biological treatment with living microbes or bio-filtration.

Table 1 shows advantages and disadvantages of the physico-chemical methods.

Table 1. Physico-chemical methods: advantages and disadvantages

Method	*Advantages*	*Disadvantages*
Co-Precipitation (alum/iron coagulation, lime softening)	▪ Relatively low cost, simple chemicals. ▪ No monitoring of breakthrough required.	▪ Toxic sludge generation and disposal on daily basis. ▪ Chemical consumables. ▪ Pre-oxidation and pH adjustment often required.
Sorption Techniques (activated alumina, iron coated sand, iron oxides, ion exchange resins)	▪ No daily sludge generation or disposal. ▪ Fewer chemical consumables.	▪ Higher cost than precipitation. ▪ Monitoring of break through required. ▪ Periodic regeneration required. ▪ pH adjustment often required.
Membrane Techniques (reverse osmosis, electrodialysis)	▪ Well defined performance. ▪ High removal efficiency. ▪ Lowest space requirements. ▪ Removal of other contaminants. ▪ No sludge generation.	▪ Greatest capital, operating and maintenance costs. ▪ Toxic wastewater concentrates. ▪ Membranes are not stable to strong oxidizers.

At the moment mining industry prefers arsenic disposal procedures that involve formation of an insoluble amorphous or poorly crystalline ferric arsenate compound; this amorphous salt is similar to arsenical ferrihydrite. Despite concerns about its long-term thermodynamic stability, arsenical ferrihydrite seems to be stable for many years in a proper environment, which includes a slightly acidic pH and oxidizing conditions. High Fe/As ratio and presence of heavy metals seem to increase the stability of arsenical ferrihydrite. High temperature operations lead to the formation of scorodite ($FeAsO_4 \cdot 2H_2O$) and/or a series of ferric arseno-sulphate compounds, depending on concentration of sulphate ions.

Scorodite has several advantages over arsenical ferrihydrite as disposal compound, including a lower iron demand, higher density and a greater thermodynamic stability. New procedures were developed to generate scorodite at ambient pressure, which would offer a significant reduction in capital cost because of elimination of the required autoclaves.

Harper and Kingham (1992) used chemical precipitation by means of alum, sodium sulphide or ferric chloride as coagulant with hydrate lime for pH adjustment. To improve As removal up to 98%, they concluded that a multiple dosage is necessary. Bhattacharyya and his group studied metal precipitation by sodium sulphide (Bhattacharyya et al., 1980). Namasivayam and Senthil Kumar (1998) studied the use of Fe(III)/Cr(III) hydroxide waste coming from an electrolytic process of fertilizer industry. Alum and ferric sulphate were also tested for arsenic removal (Gulledge et al., 1973). Tokunaga et al. (1999) found that the complete removal of As(III) is not possible, whereas the best removal was achieved with As(V): different salts were investigated (La(III), Al(III), Ca(II), Fe(III)) and Fe(III) gave the best results for both

As(III) and As(V). Hering et al. (1996) concluded that alum can not remove As(III), whereas As(III) removal by ferric chloride is influenced by the composition of source water; moreover, the presence of sulphates and organic matter negatively affected As(III) precipitation. Arsenic-containing tailings or residues create several environmental problems when stockpiled improperly; as an example, in Snow Lake, Manitoba (Canada) cyanide tailings from refractory arsenopyrite ore concentrate processing are still releasing arsenic, because of the action of water and air that has oxidized many of the original compounds and produced two different iron sulfo-arsenates, usually more stable but not in the particular reducing conditions of the pile. Groundwater collected from monitoring wells contains more than 20 mg L^{-1} total As with predominance of As(III) (Salzsauler et al., 2005).

Arsenic mobilization and speciation was also studied in the aquifers in the surroundings of a an inactive Mexican smelting plant. Calcium arsenates caused high levels of pollution, as the As in groundwater table concentration was 158 mg L^{-1} and the total As release was estimated to be around 7.5 tons per year. Free calcium ions in soil are able to control arsenic mobility in the aquifer through the diagenetic precipitation of calcium arsenates $Ca_5H_2(AsO_4)4 \cdot nH_2O$, preventing further mobilization of As (Martínez-Villegas et al., 2013).

An in situ experimental study for chemical fixation of arsenic in arsenic-contaminated subsurface soils was carried out by Yang et al. (2007). Ferrous sulfate, potassium permanganate and calcium carbonate were used alone and in combination to limit the release of arsenic. EPA method 1312 and TCLP were used for evaluation of As mobility. All treatments were found to be effective for both soils, reducing the arsenic leachability. Nevertheless, treatment with ferrous sulfate gave the best results in terms of As concentration in the leachate. Arsenic organic and inorganic chemistry in soils was well described by Sadiq (1997). Guenegou et al. (1997) studied arsenic elimination by precipitation of calcium arsenite and arsenate, as well as co-precipitation in presence of iron(III) from aqueous solutions obtained by hydrolysis of Lewisites, with 0.1 and 1 mol L^{-1} of arsenic and chloride ions, respectively. The calcium arsenite precipitation entails an arsenic precipitation yield of 80% at pH 11 and with addition of calcium ions in a molar ratio $Ca^{2+}/As3^{+}$ of 15.

Palfy et al. (1999) demonstrated that it is possible to reduce the arsenic solubility of untreated waste sludges from 6430 mg L^{-1} to 0.823 mg L^{-1} by arsenic stabilization. In particular, arsenic was precipitated and immobilized by using ferric sulphate, calcium oxide and hydrogen peroxide to oxidize As(III) into As(V). Ca/As molar ratios greater than 8 did not increase As reduction in solution; Fe/As molar ratios 4 and 6 were also tested for a reaction time of 24 h. Arsenic was thus immobilized by the addition of Portland cement to avoid long term stability problems of the precipitated salts. The same immobilization technique was used by Kundu and Gupta (2008). Addition of lime and cement showed an effective containment of As(III) within the matrix. The solidification and stabilization technique with lime and Portland cement was applied successfully to the immobilization of arsenic wastewater residuals by Camacho et al. (2009). In particular, it was also demonstrated the stabilization effect of calcium. Anyway, precipitated material obtained by the sole addition of lime is not stable over time, since the buffering effect of lime decreased by dissolution and carbonation when exposed to atmospheric CO_2. Arsenate desorption was induced by using both de-ionized water and phosphate solution and demonstrate the good stability of the precipitated material obtained by cement. Stabilization of arsenic by calcium precipitation was also investigated by Moon et al. (2004). With As(V) in solution, precipitation of $Ca_4(OH)_2(AsO_4)_2 \cdot 4H_2O$ occurred with Ca/As molar ratios greater than 1. Addition of kaolinite was also studied. In the latter case formation of $NaCaAsO_4 \cdot 7.5H_2O$ was detected in the precipitate when As was in the pentavalent form. When As(III) was precipitated, three main phases were detected in the precipitate: portlandite, calcium arsenite and calcite. Results showed that the effectiveness of both As(III) and As(V) immobilization increased with higher Ca/As molar ratios. Removal and stabilization of arsenic from industrial process solutions, sludges and solid residues is a technical problem of great importance. For instance, Yuhu et al. (2011) described a leaching process to remove selectively As from Waelz zinc oxide. The pregnant solution, containing 10.37 g As L^{-1} was treated by hydrogen peroxide followed by lime precipitation with a lime/As molar ratio equal to 3:1, at 90 °C for 2h, which removed 99.86% of arsenic, with a residual concentration of 2 mg L^{-1} in the solution. The precipitate of cristalline calcium arsenate $Ca_5(AsO_4)_3OH$ was solidified with cement and thus landfilled. Arsenic stabilization also involves copper smelter industry. Viñals et al. (2010) investigated precipitation of arsenical natroalunite, that is suitable for long-term storage, from a calcium arsenate waste coming from a copper pyrometallurgical plant. Calcium arsenate waste was leached with H_2SO_4 and ozonized at 25 °C to convert As(III) to As(V). Hydrothermal synthesis of arsenical natroalunite was carried out in a pressurised reactor at 200 °C for 2h. Leaching tests at pH 1 demonstrated a good stability of the salt obtained: the best result showed an arsenic concentration lower than 1 mg L^{-1} in the leachate.

Sturgill et al. (2000) developed a process for simultaneous recovery of arsenic and gallium from GaAs polishing waste. That process involved the removal of the majority of arsenic as a mixed precipitate of calcium arsenate. In a first step at ambient temperatures and pH greater than 11 by using NaOH, arsenic precipitated and gallium remained in solution. Hence, gallium hydroxide was precipitated in the second process stage through pH adjustment to 6-8 with sulphuric acid.

The influence of calcite ($CaCO_3$) in sequestration of arsenic is also known (Winkel et al., 2013). Furthermore, the role of calcium ions is also described in the analysis of arsenic and selenium leaching of bituminous coal ash and following precipitation (Wang et al., 2009). In the present work removal of As(III) and As(V) from acid and neutral solutions was investigated. These solutions simulate typical arsenic concentrations resulting from a wet scrubber of flue gas coming from roasting processes of auriferous ores; it is well know that such ores are mainly composed by sulphides and arsenic is often present as well. This work was carried out in the ambit of a project for recovery of gold from auriferous arsenopyrite deposit in Lazio region, Italy: after grinding, such ore undergoes thermal oxidation at temperatures around 700 °C, in order to remove sulphur, and the sublimated arsenic is captured by a wet scrubber together with SO_2. Hence, arsenic has to be removed and deactivated for safe disposal. Flue gas emissions from roasting processes have to be treated before releasing into the atmosphere, according to the best and effective technologies. The Italian decree D.P.R. 24 May 1988, n.203 reports air quality regulations and it disciplines all emissions (solid, liquid and gaseous) produced by industrial plants. The D.Lgs. 152/2007 lists the limit of emission, whereas the D.Lgs. 152/2006 reports criteria for sampling and analysis.

The aim of this experimental work was to study how CaO, $FeCl_3$ and sulphate ions concentrations affect the precipitation of arsenic. In fact, it is of primary importance to obtain arsenic compounds chemically stable that can be disposed of in a safe way, avoiding release into soil, groundwater table or water bodies. When Fe^{3+} ions are present in solution at high pH, arsenic precipitation by calcium is improved by the adsorption effect of $Fe(OH)_3$, which acts as coagulant with a large surface area.

2. Experimental

Precipitation tests were performed by four synthetic solutions containing As(III) or As(V). Two solutions were prepared by addition of As_2O_3 (chemical grade 99.95%, Sigma-Aldrich) or As_2O_5 (chemical grade 99%, Sigma-Aldrich) in 2 L of 0.1 M H_2SO_4 solution (acid tests). The concentrations were those obtained by dissolving a weighted amount of both As_2O_3 and As_2O_5 in the two different solutions, i.e. neutral and acid; these concentrations are representative of the typical ones that can be found in wet scrubber wastewater that treats flue gas from thermal oxidation of sulphide/arsenic-containing ores. Hence, before performing the precipitation tests, the four solutions were filtered by a vacuum pump (Millipore) and analyzed by atomic adsorption spectrometry (AAS) to determine the effective concentration of As(III) or As(V); in fact, in such conditions As(III) has a low solubility and the total amount was not dissolved. The real concentrations measured by AAS were used to evaluate the precipitation yields.

The precipitation tests were carried out in 250 mL screw flasks at constant temperature in a water bath mechanically stirred (Dubnoff, ISCO) at 200 rpm. There is a significant effect on kinetics of scorodite precipitation by varying the temperature from 80 ℃ up to the boiling point of the solution (Singhania et al., 2005), so that the temperature was set at 80 ℃.

The same experimental procedure was carried out (see Table 3 for acid tests and Table 4 for neutral tests) for all solutions: a series of flasks was filled with 100 mL of solution containing As(III) or As(V) and a different amount of CaO (reagent grade, Fluka) was added to each flask.

Several samples were taken at 5, 15, 45, 90 and 120 minutes, centrifuged at 5000 rpm and analysed for arsenic determination by AAS (Varian, spectrophotometer Spectra AA-200). pH was measured by a digital pH-meter (Mettler Toledo MP220). Acid tests were replicated with the addition of 5 g L^{-1} of $FeCl_3{\cdot}6H_2O$ (97% grade, Fluka) as coagulant (see Table 5). The X-ray diffraction analysis (XRD) was carried out by a Philips PW 1830 diffractometer in order to establish the crystalline phases present in some of the precipitated samples, in order to confirm theoretical precipitation data.

3. Results and Discussion

A brief introduction to the chemistry of the aqueous system is shown as follows. A comparison between the solubility constant (K) and the activity product (Q) permits to understand whether the acid or neutral solution at 80℃ are undersaturated (Q<K), at equilibrium with Q=K or oversaturated (Q>K) in presence of a particular mineral.

Table 2 shows the mineral saturation index (SI) at different pHs:

$$SI = \log (Q) - \log (K) \tag{1}$$

These values were calculated by Phreeqc Interactive 2.14.3 software, in acid condition (H_2SO_4 0.1 M), arsenic 1 g L^{-1}, CaO 1 g L^{-1} and $FeCl_3$ 5 g L^{-1} as software input data.

Table 2**.** Saturation index of minerals in acid solution (H_2SO_4 0.1 M) with CaO (12 g L^{-1}) and $FeCl_3$ (5 g L^{-1}) at different pHs

As(III)					As(V)				
	pH 1	pH 4	pH 8	pH 12		pH 1	pH 4	pH 8	pH 12
Arsenolite	-3.13	-3.09	-3.52	-10.7	As_2O_5(cr)	-11.03	-14.45	-25.23	-44.24
As native	-7.45	-16.43	-28.64	-44.23	$Ca_3(AsO_4)_2$	-24.46	-10.06	3.15	8.03
Claudetite	-3.13	-3.09	-3.52	-10.7	$Fe(OH)_{2.7}Cl_{0.3}$	1.73	7.39	8.25	3.38
$Fe(OH)_{2.7}Cl_{0.3}$	1.73	7.39	8.25	3.37	$Fe(OH)_3$(a)	-5.52	1.03	3.09	-0.58
$Fe(OH)_3$(a)	-5.52	1.03	3.09	-0.58	Goethite	2.03	8.58	10.63	6.97
Goethite	2.03	8.58	10.63	6.97	Hematite	6.28	19.39	23.49	16.17
Hematite	6.28	19.39	23.49	16.16	Jarosite	-0.36	9.12	-0.71	-27.7
Jarosite	-0.36	9.12	-0.71	-27.7	Maghemite	-7.63	5.47	9.58	2.26
Maghemite	-7.63	5.47	9.57	2.25	Scorodite	-2.93	1.91	-1.43	-14.6

It is possible to notice that all As(III) minerals show a negative SI: this means that the solution is in undersaturated conditions with respect to those minerals. As regards As(V), $Ca_3(AsO_4)_2$ shows a positive SI at pH 8, thus oversaturated conditions occurred at alkaline pHs. Scorodite has a positive SI at pH 4, whereas at different pHs the SI is negative: this means that this compound can precipitate and solubilized again when pH increased. In our system other possible minerals containing As(V) and As(III) such as rauenthalite ($Ca_3(AsO_4)_2 \cdot 10H_2O$) and calcium arsenite ($CaHAsO_3$) are not present, as for instance in other more complex aqueous systems (Cornelis et al., 2008).

3.1 Acid Tests

Precipitation tests of arsenic from 0.1 M sulphuric acid solutions were performed by CaO with or without addition of $FeCl_3$ as coagulant. The aim of these tests was to check the effect of sulphate ions on As precipitation, as they simulated a process for treatment of wet scrubber's spent solutions used to remove arsenic from flue gas. As a matter of fact, flue gas coming from roasting of auriferous ore usually contains great amounts of arsenic and SO_2.

Table 3 shows the initial concentration of As(III) and As(V) measured by AAS and the CaO/As ratio.

Table 3. Experimental conditions of acid tests carried out without addition of $FeCl_3$; temperature 80 ℃

Treatment	As ion	As, mg L^{-1}(measured)	CaO, g L^{-1}	g CaO/g As	pH (2h)
1	As (III)	432	0	0.0	1.52
2	As (III)	432	1	2.3	1.56
3	As (III)	432	5	11.6	1.83
4	As (III)	432	7	16.2	10.61
5	As (III)	432	10	23.1	11.61
6	As (III)	432	12	27.8	11.63
7	As (V)	1046	0	0	1.52
8	As (V)	1046	1	1	1.56
9	As (V)	1046	5	5	1.83
10	As (V)	1046	7	7	10.61
11	As (V)	1046	10	10	11.61
12	As (V)	1046	12	12	11.63

As it can be inferred from Table 3, As(III) is less soluble than As(V) even in acid medium. pH of reference samples (0 g L^{-1} of CaO, treatments 1 and 7) was about 1.5. pHs were almost constant during the tests (data not shown here).

pH of treatments 2 and 3 did not change with respect to the reference sample, whereas in the remaining treatments the pH achieved values around 11. Treatments 4, 11 and 12 showed a slow kinetics and the equilibrium pH was reached after 90, 45 and 15 minutes, respectively. In the other treatments the equilibrium pH was already reached after 5 minutes. Figures 1 and 2 show the concentration trend of As(III) and As(V), respectively. The reference sample containing 0 g L^{-1} of CaO shows that the solubility of As(III) decreases with time (Fig.1), instead, it is constant for As(V) (Fig.2). These results indicate that the greater the amount of CaO, the higher the process kinetics. Furthermore, As(III) showed better precipitation kinetics than As(V).

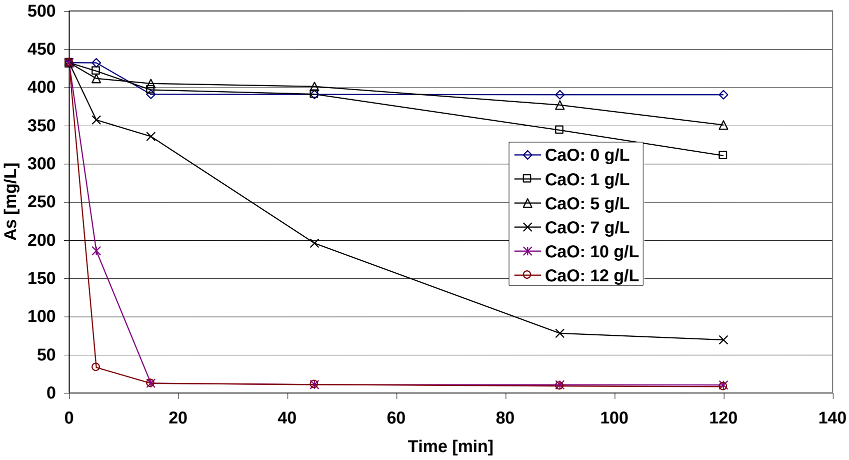

Figure 1. As(III) concentration vs time (treatments 1÷6 in Table 3: reference value 0 g L^{-1} of CaO).

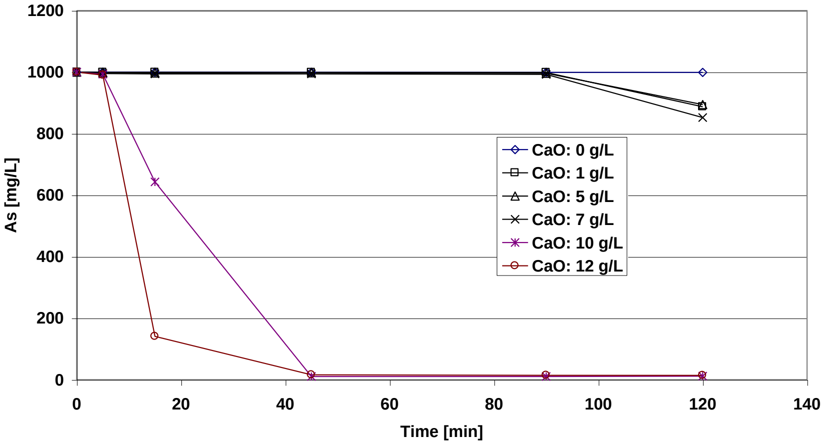

Figure 2. As(V) concentration vs time (treatments 7÷12 in Table 3: reference value 0 g L^{-1} of CaO, dotted line).

Figure 3 reports arsenic precipitation yields at two different times for each treatment; it is possible to notice that after 5 minutes As(V) is not removed whereas As(III) removal yield is around 92% with 12 g L^{-1} of CaO. Increasing process time the precipitation yields increase until 98% for both As(III) and As(V) when the highest CaO concentration is present, i.e. 12 g L^{-1}.

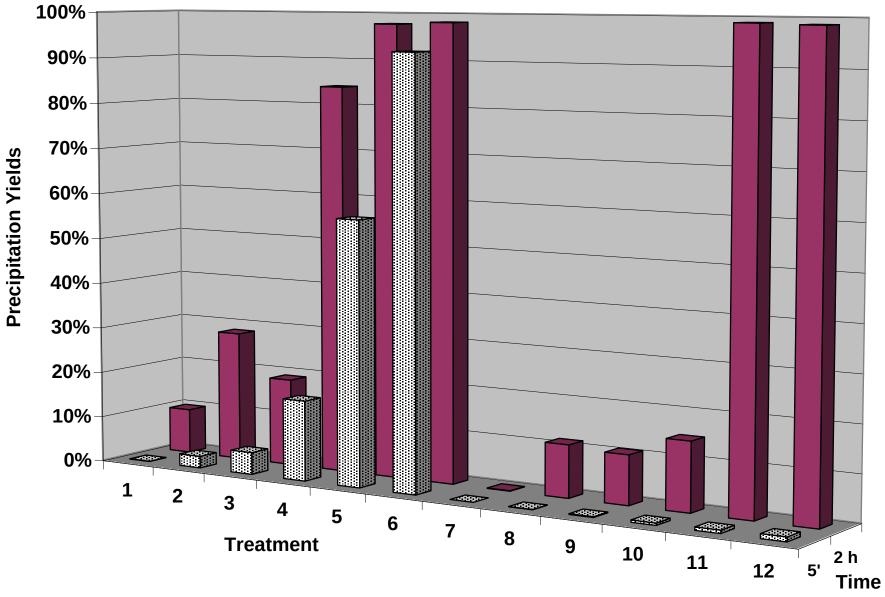

Figure 3. Arsenic precipitation yields at two different process time, treatments without $FeCl_3$ (treatments 1÷12 in Table 3).

Those treatments described before were repeated by addition of 5 g L^{-1} of ferric chloride. Table 4 reports the experimental plan.

Table 4. Experimental conditions of acid tests carried out with $FeCl_3$ (5 g L^{-1}); temperature 80 ℃

Treatment	As ion	As, mg L^{-1}(measured)	CaO, g L^{-1}	g CaO/g As	pH (2h)
13	As (III)	180	0	0.0	1.19
14	As (III)	180	5	27.8	1.48
15	As (III)	180	7	38.9	1.67
16	As (III)	180	8	44.4	1.67
17	As (III)	180	9	50.0	1.68
18	As (III)	180	12	66.7	1.83
19	As (V)	1073	0	0	1.16
20	As (V)	1073	5	5	1.71
21	As (V)	1073	7	7	1.67
22	As (V)	1073	8	8	1.77
23	As (V)	1073	9	9	1.80
24	As (V)	1073	12	12	1.90

The addition of ferric chloride does not have any effect on As(V) concentration. The initial concentration of As(III) is lower than that of As(III) measured in the solution without $FeCl_3$, i.e. 180 mg L^{-1} against 432 mg L^{-1}. This means that in this range of pH ferric chloride reduces the solubility of As(III) whereas does not influence the solubility of As(V).

In these treatments (data not reported) the equilibrium pH value is reached after 5 minutes and remains constant throughout the tests, but the pH increment is not so high as in the other treatments, where the final pH is close to 11. The pH of the reference sample is around 1.2, whereas the pH of treatments 13-24 ranges from 1.5 to 2.

Figures 4 and 5 show the concentration trends of arsenic. In the reference test, As(III) concentration decreases with time, as in the previous tests. It can be inferred from Figures 4 and 5 that As(V) precipitation kinetics is faster than that of As(III).

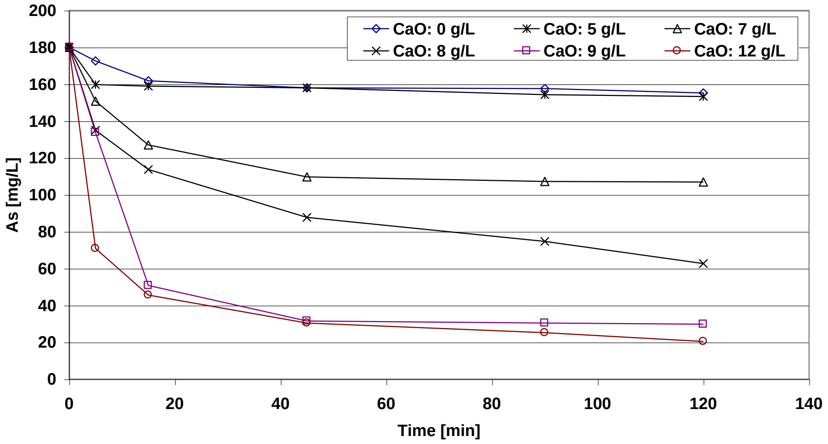

Figure 4. As(III) concentration vs time (treatments 13÷18 in Table 4: reference value 0 g L^{-1} of CaO).

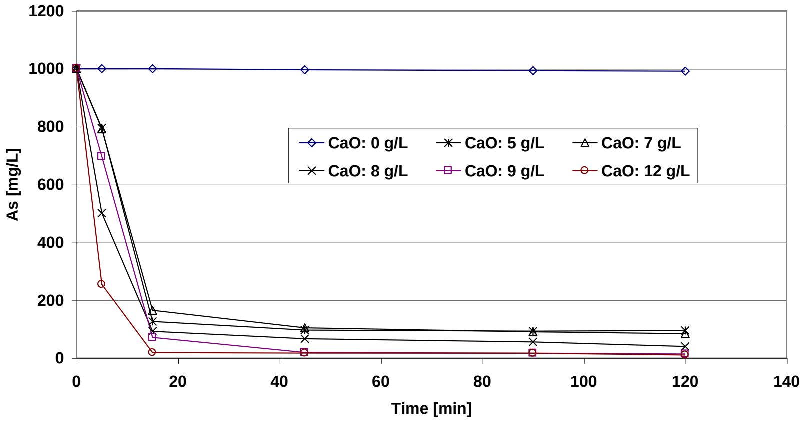

Figure 5. As(V) concentration vs time (treatments 19-24 in Table 4: reference value 0 g L^{-1} of CaO, dotted line).

Figure 6 shows arsenic precipitation yields at two different process times for every treatment. It is possible to note that most of As(V) is already removed after 5 minutes (75% with 12 g L^{-1} of CaO) because of ferric chloride; As(III) yield is about 60% by using the same amount of CaO, so that the removal is lower than that obtained in the test without coagulant. When the process time increases the precipitation yields increase up to 88% and 99% for As(III) and As(V), respectively.

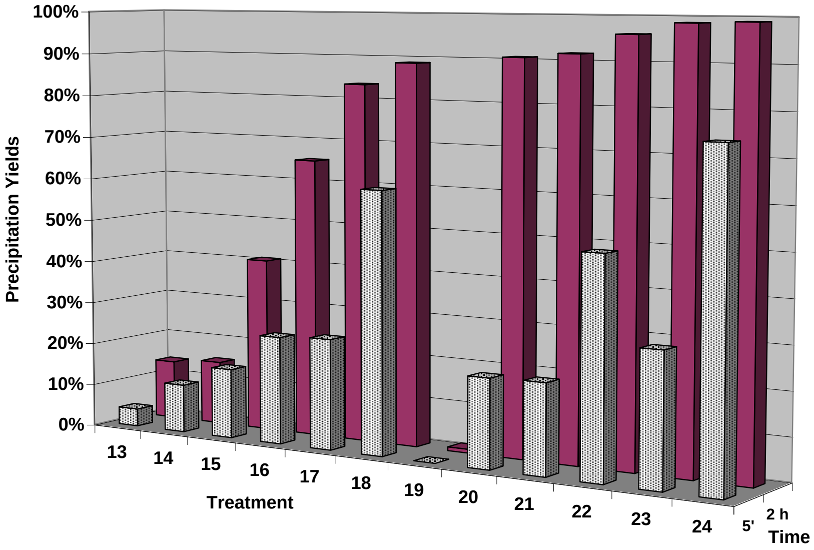

Figure 6. Arsenic precipitation yields at two different process time, treatments with $FeCl_3$ (5g L^{-1}, treatments 13-24 in Table 4).

Figure 7 shows the precipitation yields for those treatments carried out with and without ferric chloride, keeping constant the amount of CaO (see tables 3 and 4 for experimental conditions). The precipitation yield of As(III) decreases when the coagulant is added and this is true for every CaO concentration. In treatment 6, As concentration is around 8 mg L^{-1} and the precipitation yield close to 98% after 2 h, whereas in treatment 18 the concentration of As is more than double, i.e. nearly 20 mg L^{-1}.

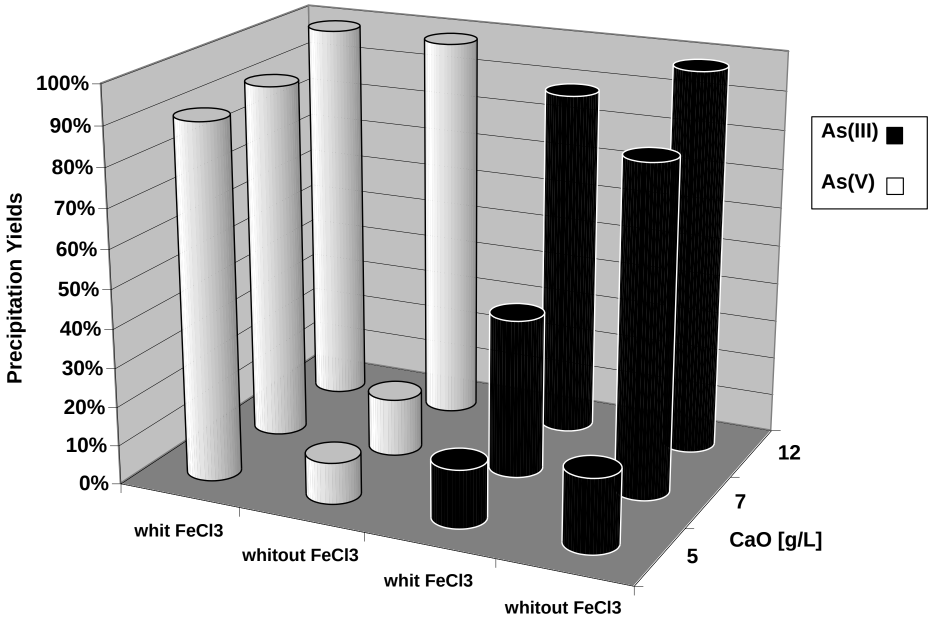

Figure 7. Arsenic precipitation yields after 2 h: comparison of treatments carried out with and without ferric chloride with the same CaO concentration.

On the contrary, the coagulant is able to increase the removal of As(V). As a matter of fact, in treatment 9 (5 g L^{-1} of CaO) the removal yield is only 10% (As 895 mg L^{-1}), whereas in the corresponding treatment 20 this value increases up to 90% (95 mg L^{-1}). It is possible to conclude that $FeCl_3$ has a double effect: it improves the kinetics of As(V) precipitation and decreases the precipitation of As(III). As regards acidic tests, the following conclusions can be drawn:

- As(III) and As (V) removal becomes significant (>80%) when CaO concentration is greater than 7 g L^{-1} and 10 g L^{-1}, respectively;

- As(V) shows slow kinetics with respect to the As(III) one. This means that the process time required to obtain high As(V) removal yields is higher than that necessary for the same yield of As(III);

- in the best operating conditions investigated in this work the As removal yield is about 99% for both arsenic valences;

- $FeCl_3$ reduces the initial solubility of As(III) but, at the same time, reduces the kinetics of As(III) precipitation. This effect produces an increase of As concentration at the end of the process and consequently the removal yield decreases (<90%);

- $FeCl_3$ promotes precipitation kinetics of As(V): after 2 h the precipitation yield is greater than 90% for each treatment. This is due to formation of scorodite, that has a very low solubility in aqueous solution. XRD analysis confirmed this hypothesis, since the precipitate was mainly represented by such compound.

3.2 Neutral Tests

Precipitation tests of arsenic in aqueous solution were performed by addition of CaO at 80 ℃. Table 5 shows the real initial concentration of As(III) and As(V), the concentration of CaO as well as the CaO/As ratio. In this study the new tests were numbered in succession.

Table 5. Experimental conditions of neutral tests carried out without addition of $FeCl_3$; temperature 80 ℃

Treatment	As ion	As, mg L^{-1}(measured)	CaO, g L^{-1}	g CaO/g As	pH (2h)
25	As (III)	340	0	0.0	5.59
26	As (III)	340	0.5	1.5	10.28
27	As (III)	340	1	2.9	11.26
28	As (III)	340	2	5.9	11.50
29	As (III)	340	5	14.7	11.65
30	As (V)	10215	0	0	1.41
31	As (V)	10215	0.2	0.02	1.51
32	As (V)	10215	0.5	0.05	1.54
33	As (V)	10215	1	0.1	1.67
34	As (V)	10215	5	0.5	2.52
35	As (V)	10215	10	1	4.38
36	As (V)	10215	12	1.2	4.53
37	As (V)	10215	15	1.5	4.75
38	As (V)	10215	40	4	11.45

pH of reference samples (treatments 25 and 30) is 6.50 and 1.35, respectively. The other pH values are not reported here. This means that As_2O_5 shows acid behaviour with respect to As_2O_3. In fact, after 5 minutes with 5 g L^{-1} of CaO the pH increment is 5 for As(III) and 1.1 for As(V). pH is rather constant for nearly all tests and the equilibrium value is already reached after 5 minutes. In treatment 35 the equilibrium value is achieved after 1 h. Equilibrium pHs range from 10 to 12 in treatments 26-29 and from 2.5 to 5 in treatments 34-37. pH of treatments 31-33 does not change with respect to the value of the control sample, whereas pH of treatment 38 is around 12.

Figures 8 and 9 show the concentration trend of As(III) and As(V), respectively. The reference sample having 0 g L^{-1} of CaO highlights that the solubility of As(III) decreases during the test (Fig.8), as well as that one of As(V) (see Fig.9). Moreover, the initial precipitation kinetics of As(III) does not depend on CaO concentration and the process kinetics of As(V) increases with the amount of CaO.

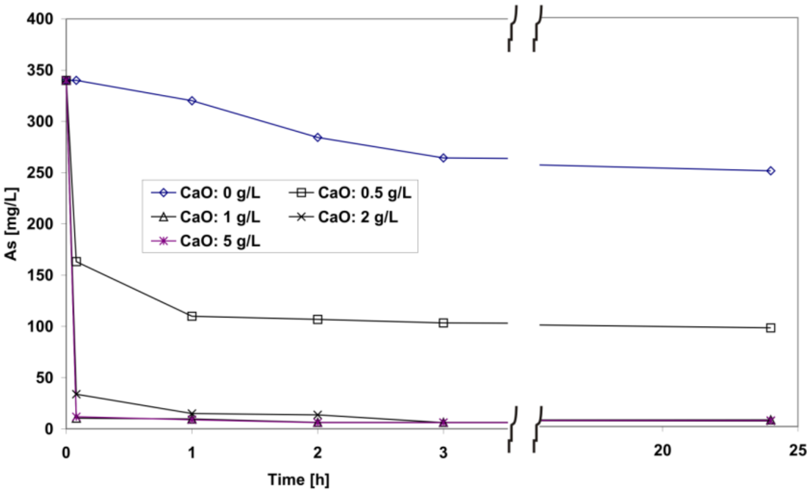

Figure 8. As(III) concentration vs time (treatments 25-29 in Table 5: reference value 0 g L^{-1} of CaO).

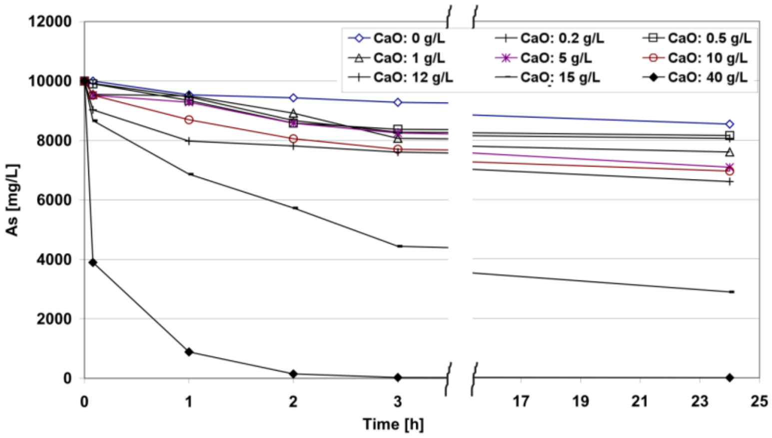

Figure 9. As(V) concentration vs time (treatments 30-38 in Table 5; reference value 0 g L^{-1} of CaO, dotted line).

These trends show that it is possible to achieve precipitations greater than 70% with addition of CaO only (Ahmed, 2016). Moreover, oxidation of As(III) to As(V) seems not to be required, as stated in many of the literature papers. Thus, use of an oxidant that leads to greater operating costs is not required in industrial facilities. Figure 10 shows arsenic precipitation yields at three different process times for each treatment. It is possible to note that after 5 minutes and with a constant amount of CaO, As(V) is not removed (only 1%), whereas As(III) yield is around 52% (treatments 26 and 32). This yield increases when CaO concentration raises. Furthermore, the higher the process time, the greater the precipitation yield. Using the highest concentration of CaO (5 g L^{-1}) in treatments with As(III), the removal is nearly 98% after 2 h. As(V) removal with 5 g L^{-1} of CaO is 14% only after 2 h and becomes 29% after 24 h. This means that a significant As(V) removal can only be obtained if CaO concentration is increased to 40 g L^{-1} (treatment 38); these operating conditions assures an As precipitation of 99% after 2 h and 100% after 24 h.

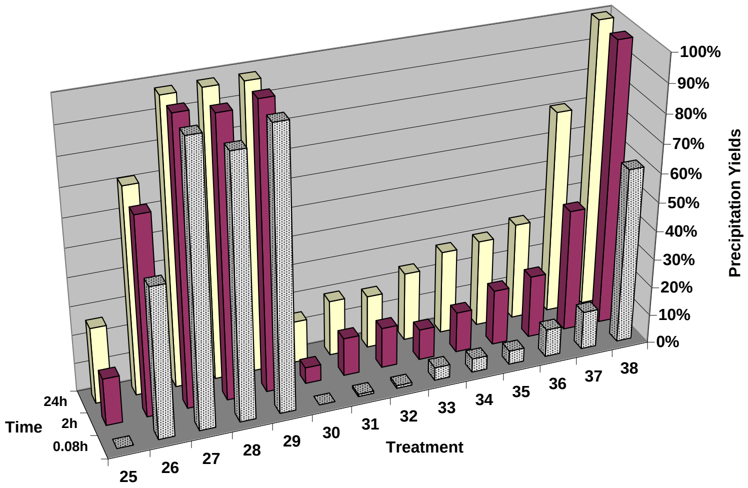

Figure 10. Arsenic precipitation yields at three different process times (treatments 25-38 in Table 5).

Figure 11 shows the arsenic precipitation yields for acid, acid with coagulant and neutral treatments. The most efficient process for As(III) seems to be that one carried out in neutral solution (98% yield), whereas the best result for As(V) was obtained in the process carried out by the acid solution with coagulant (90%). From the results it can be inferred that Fe^{3+} ions enhance the precipitation of As(V) because of scorodite formation, according to the reaction:

$$AsO_4^{3-} + Fe^{3+} + 2\ H_2O \rightarrow FeAsO_4 \cdot 2H_2O\downarrow \qquad (2)$$

Scorodite has a very low solubility, since the solubility product K_{sp} is 10^{-24}. A secondary reason could be the formation of electrostatic binding of soluble arsenic onto the external surface of such coagulant that strongly improves As(V) precipitation. Figures 12a and 12b show the solubility of the species which are part of the investigated aqueous system and the predominance areas of solid precipitates that can occur in the same system. Those diagrams were developed by Hydra-Medusa software package, specific to draw chemical equilibrium diagrams.

Regarding As(III), the different behaviour obtained with respect to As(V) could be due to deprotonation reaction: after being dissolved in water, $FeCl_3$ gives the hexaaquo iron(III) ion in solution, which would react as follows:

$$FeCl_3 \rightarrow Fe^{3+} + 3\ Cl^- \qquad (3)$$

$$[Fe(H_2O)_6]^{3+} + H_2O \leftrightarrow [Fe(H_2O)_5(OH)]^{2+} + H_3O^+ \qquad (4)$$

$$[Fe(H_2O)_5(OH)]^{2+} + H_2O \leftrightarrow [Fe(H_2O)_4(OH)_2]^+ + H_3O^+ \qquad (5)$$

Salts from transition metals form hydrated ions in aqueous solution: hence, the presence of H_3O^+ ions makes the solution acidic. Additional H_3O^+ ions are neutralized by OH^- coming from $Ca(OH)_2$: such anions are thus consumed and do not take part to precipitation of As(III) when pH decreases. Furthermore, precipitation of both As(III) and As(V) in acidic medium is lower with respect to the neutral one since sulphuric acid is completely split in solution: this leads to precipitation of $CaSO_4{\cdot}2H_2O$, so that less Ca^{2+} ions are available for removal of arsenic.

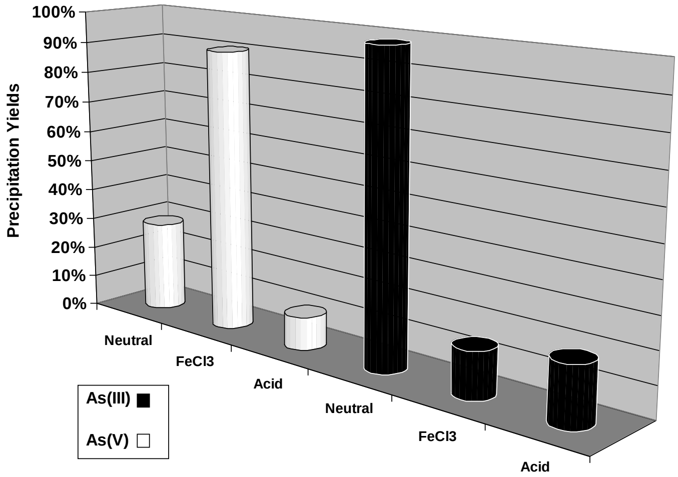

Figure 11. Arsenic precipitation yields after 2 h: yields of acid, acid with $FeCl_3$ and neutral treatments with the same CaO concentration (5 g L^{-1}).

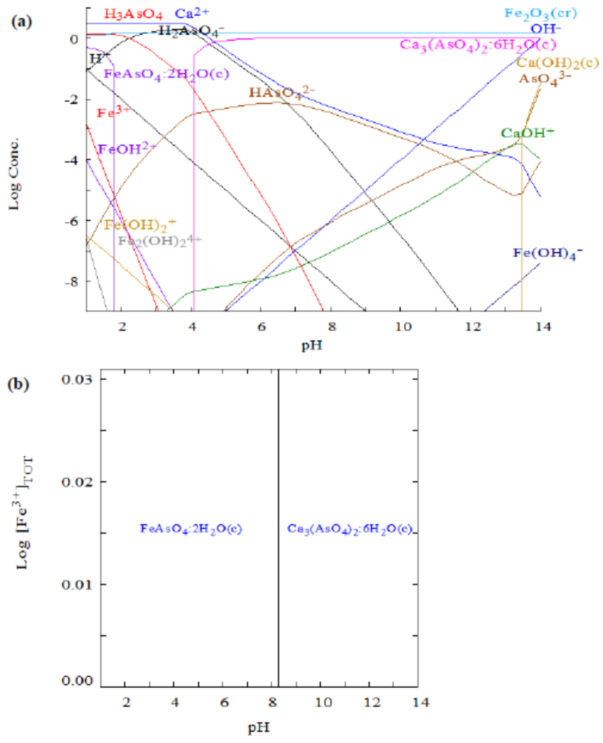

Figure 12). Concentration of salts and ions vs pH of the aqueous solution investigated (a) and solid precipitates (b)

4. Conclusions

In this paper several precipitation tests were carried out to evaluate the best process to remove arsenic from aqueous solutions. The experiments were performed by solutions containing As(III) or As(IV), some of these acidified by sulphuric acid to simulate the dissolution of SO_2 in treatment of flue gas from roasting processes of sulphide ores. Different amounts of CaO were added to some solutions, whereas in some experiments iron chloride was also tested to study the influence on As precipitation.

In the acidic tests the initial solubility of As(III) without CaO is strongly influenced by $FeCl_3$: this compound indeed reduces the As(III) solubility and at the same time slows down the kinetics of precipitation when CaO is added. On the contrary, the precipitation kinetics of As(V) is improved when iron chloride is added. Without $FeCl_3$, As(III) and As(V) removal becomes significant when CaO concentration is greater than 7 g L^{-1} and 10 g L^{-1}, respectively. In the experiments with iron chloride, a precipitation yield greater than 80% is obtained with 9 g L^{-1} and 5 g L^{-1} of CaO for As(III) and As(V), respectively. From these results it can be inferred that $FeCl_3$ has a negative effect on As(III) removal; on the contrary, there is a clear positive effect of $FeCl_3$ on As(V) removal

Nearly 98% of As(III) was removed with 10 g L^{-1} of CaO after 15 minutes, whereas 12 g L^{-1} are necessary to remove 95% of arsenic after 2 h when $FeCl_3$ is added.

99% of As(V) is removed with 10 g L^{-1} of CaO after 45 minutes, with or without iron chloride; however, when iron chloride is present, 5 g L^{-1} of CaO and 45 minutes are enough to remove about 90% of As(V).

Sulphuric acid has shown a positive effect on As(V) removal; in fact, in the neutral experiments 40 g L^{-1} of CaO and 1 h are necessary to precipitate 90% of As. The same yield is obtained for As(III) with only 5 g L^{-1} of CaO after 5 minutes.

When comparing the acid and neutral series of tests, it can be highlighted that the medium in which As is dissolved influences the precipitation process: in fact, As(III) precipitation is much more efficient in neutral conditions, i.e. in water without sulphate ions. Moreover, iron chloride improves As(V) removal but reduces that one of As(III). This research is a preliminary work that will help in designing and implementing the treatment of wet scrubbing wastewater from the flue gas of the roasting pilot-plant that will be constructed in the next months.

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