

Hydrometallurgical extraction of tin from cassiterite ore in Kalima (DR Congo) by alkaline fusion with eutectic mixture of alkali hydroxides (sodium and potassium)

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Abstract: In this study, it was possible to optimize the hydrometallurgical extraction conditions of tin from cassiterite ore in Kalima (DR Congo) by an alkaline smelting process with an equimassic mixture of NaOH and KOH. This ore was characterized by a 68.58% tin content in a siliceous gangue incorporating other elements such as iron, calcium, potassium and titanium.

Smelting was carried out at an ore/(NaOH+KOH) ratio of 1/5 in a molten mixture at 350°C for 90 minutes to form soluble M_2SnO_3 (M = Na or K) and also $M_8SnSi_6O_{18}$ (S) insoluble in water. The roasted solid/liquid ratio of 1g/10 ml was sufficient to leach more than 96% by weight of tin for 30 minutes at room temperature (25°C). The leached solution was characterized by a pH of 9.7 with the presence of the species $Sn(OH)_6^{2-}$ and $Sn(OH)_5^-$. With this eutectic mixture, the melting temperature was almost halved and a higher yield was achieved compared to traditional approaches to hydrometallurgical tin extraction.

Key Word: Tin hydrometallurgy, cassiterite smelting, molten alkali hydroxides

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I. Introduction

Metallic tin is used in several industrial and domestic applications such as the tinning of other common metals (iron, copper,...), manufacture of appliances and piping for the food industry, alembic tops, refrigeration appliances, industrial tubs, welding rods, ornamental or tableware, toys, organ pipes,... It is also used in the form of flexible tubes or thin sheets. In D.R. Congo, tin is found in the form of several minerals, the main one being cassiterite mined in the Eastern provinces where Kalima is one of the exploitation centres of Maniema.

The extractive metallurgy of tin poses many problems in relation to its affinity with iron and silicon (Grant, 2001). In relation to the types of tin ores, oxidised or sulphide, the literature lists several industrial techniques for extracting tin based on the chemical composition of the ore to be processed (Habashi, 1997; Gostishchev, et al., 2008). These include pyrometallurgical and hydrometallurgical techniques. Pyrometallurgy of tin presents many difficulties: excessive energy consumption (Murach, et al., 1964), iron is often bonded to reducing molten tin (Zijian, et al., 2017), the combination of tin oxide with silica reduces the amount of metallic tin expected (El Deeb, et al., 2015), etc..

The hydrometallurgical recovery scheme for tin ores comprises two distinct phases: leaching of the ore with the objective of solubilising a concentrate or reject containing tin and solvent extraction of the metal contained in the latter. Because cassiterite is resistant to attack by traditional solvents, whether acidic or basic, no process for leaching tin from its concentrates has been developed on an industrial scale (De Cuyper, 1995).

However, several routes have been proposed but have not progressed beyond the laboratory stage (Fecko, et al., 2011; Cheng, et al., 2011; Jha, et al., 2012; Havalik, et al., 2011). Some involve direct leaching under severe conditions (high temperature and sometimes high pressure) in media such as HCl, Na₂S. Others precede the leaching with an oxidizing screen to remove sulphur, followed by a reducing melt at 1300-1400°C, followed by quenching with water to obtain a glassy phase in which the tin oxide is leachable by H₂SO₄ without attacking the silicate structure (Pearson, et al., 1977).

The only industrial applications of hydrometallurgy in the treatment of tin ores and concentrates are in the purification of concentrates. These are sulphur leaching to dissolve iron carbonates, hydrochloric pressure leaching at 110°C to dissolve impurities such as iron, copper, arsenic, bismuth, and leaching in carbonate or ammoniacal media to remove tungsten present in the form of scheelite (CaWO₄) (De Cuyper, 1995; Thongbo, et al., 2010; Bunnakha, et al., 2012). Other researchers have studied the contribution of magnetite to tin reduction in the CO-CO₂-rich atmosphere; results showed that magnetite contributed to reduced tin volatilization and

spinel (Fe-Sn) transformation of cassiterite but at temperatures of 850° to 1000°C. This is the case when smelting occurs in the NaCO₃-NaNO₃ salt system and the coal mixture of anthracite (imported) and Enugu coal (Zhang, et al., 2016; El Deeb, et al., 2015; Ayeni, et al., 2013). Tin smelting applications present many problems such as higher melting temperature, long melting time and high leakage of some tin through volatilization (Mutombo, et al., 2018).

In order to meet the needs of the various industries that have to satisfy economic demands, a study to optimise the parameters for the solution of tin from cassiterite ore by alkaline smelting with the eutectic mixture of alkaline molten hydroxides (NaOH and KOH), under low temperature conditions, was envisaged. Consequently, the main objectives in this work were to determine the effects of alkaline smelting with the eutectic mixture of NaOH and KOH on the tin leaching yield in order to optimize certain parameters such as: (1) quantities of fluxes and ore; (2) melting temperature, (3) melting time; (4) volume of leachant; (5) leaching temperature and (6) leaching time.

II. Material And Methods

2.1. Materials

The approximately 15 kg cassiterite ore used in this work was found in artisanal mining quarries in Kalima (DRC). This ore was processed to a grain size of less than 75 µm for use in chemical (X-ray fluorescence spectrometry) and mineralogical (optical microscopy and X-ray diffraction) analyses and for smelting tests. The reagents used, NaOH, KOH and HNO₃, were chemically pure.

2.2. Methods

2.2.1. Merger processes

A mass of the treated sample was mixed with the fluxes (NaOH and KOH) in varying mass proportions. This mixture was placed in the oven at 105°C for drying for 3 hours. The dried mixture was placed in a porcelain crucible and placed in the electric furnace for melting. This melting was done at given variable temperatures (150°, 200°, 250°, 300°, 350°, 400°, 450°, 500°, 650°, 700°, 750° and 800°C) and times (15, 30, 45, 60, 75, 90, 105 and 150 min). Afterwards, the roasted products were cooled in an ambient atmosphere before being used for further testing and analysis.

2.2.2. Leaching process

10 g of the melted and cooled sample were leached at 300 rpm of stirring with a fixed volume of water (25, 50, 75, 100, 125 and 150 ml) in a 500 ml round flask placed in a water bath set at a given temperature (25°, 30°, 35°, 40° and 45°C) and for a given time (20, 30, 40, 50 and 60 minutes). Filtration took place to separate the filtrate and the residues. These residues were washed with distilled water to identify, based on elemental contents (XRF), the mineral phases that resisted solution. The leaching filtrate was characterized by element contents in solution and a pH which was subsequently modified by the addition of HNO₃ or NaOH, depending on the pH value of the start, in order to study the behaviour, in relation to the pH variation, of the form of tin which was in solution. Before and after each addition of HNO₃ or NaOH, the pH and the element contents were determined using the pH meter and the Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES) respectively.

The leaching efficiency was evaluated using the following relationship:

$$\text{Rdt}_x(\%) = \frac{(\mathbf{M}_{\text{EF}} \cdot \mathbf{T}_{\text{xEF}} - \mathbf{m}_{\text{R}} \cdot \mathbf{T}_{\text{xR}})}{\mathbf{M}_{\text{EF}} \cdot \mathbf{T}_{\text{xEF}}} \times 100$$

where $\text{Rdt}_x(\%)$ is the leaching yield of element x, \mathbf{M}_{EF} is the mass (gr) of the molten sample, \mathbf{T}_{xEF} is the content (%) of element x in the molten sample, \mathbf{m}_{R} is the mass (gr) of the leaching residue and \mathbf{T}_{xR} is the content (%) of element x in the leaching residue.

III. Results and discussion

3.1. Characterisation of the sample

The elemental chemical analysis, by XRF, of the tin concentrate showed in Table 1 the presence of eleven major elements (>0.1%) to which tin was considered the abundant element followed successively by silicon, iron, calcium, potassium, titanium, tungsten, aluminium, manganese, magnesium, niobium and tantalum. The other elements were found in trace amounts. In terms of elemental oxides, tin oxide alone accounted for 73.21%, followed by silicon (7.39%), iron (5.05%) and calcium (3.35%); while the others achieved 6.90% with a loss on ignition (P.F.) of 4.10%, as shown in Table 1.

Light microscopy revealed, in Figure 1, the presence of cassiterite (SnO₂), quartz (SiO₂) and phyllite [KCa(Al₃Si₅O₁₆).6H₂O]. The X-ray diffraction pattern shown in Figure 2 showed peaks of several minerals such as cassiterite SnO₂, wadginitite Mn(Sn, Ta)(Nb, Ta)₂O₈, qitianlingite (Fe₂Nb₂WO₁₀), wollastonite (CaO.SiO₂) and

galena (PbS). The two mineralogical analysis techniques used gave results that confirm that this sample came from deposits associated with albitized or greisenified granitic domes in which pegmatites and quartz veins develop because moderate development of sulphides (PbS) has been observed (Lepersonne, 1968; Varlamoff, 1953).

Table 1. Chemical composition of cassiterite concentrate

Elements	Fe	Mn	Si	Nb	Ta	Sn	W	K	Ca	Al	Ti	P.F.
Grade	3,87	0,21	3,99	0,14	0,18	68,58	0,31	1,85	2,79	0,16	0,78	-
Oxides	F ₃ O ₄	MnO ₂	SiO ₂	Nb ₂ O ₅	Ta ₂ O ₅	SnO ₂	WO ₄	K ₂ O	CaO	Al ₂ O ₃	TiO ₂	-
Grade	5,05	0,48	7,39	0,59	0,71	73,21	0,74	2,72	3,35	0,63	1,03	4,10



Figure 1. Light microscopic analysis of the sample

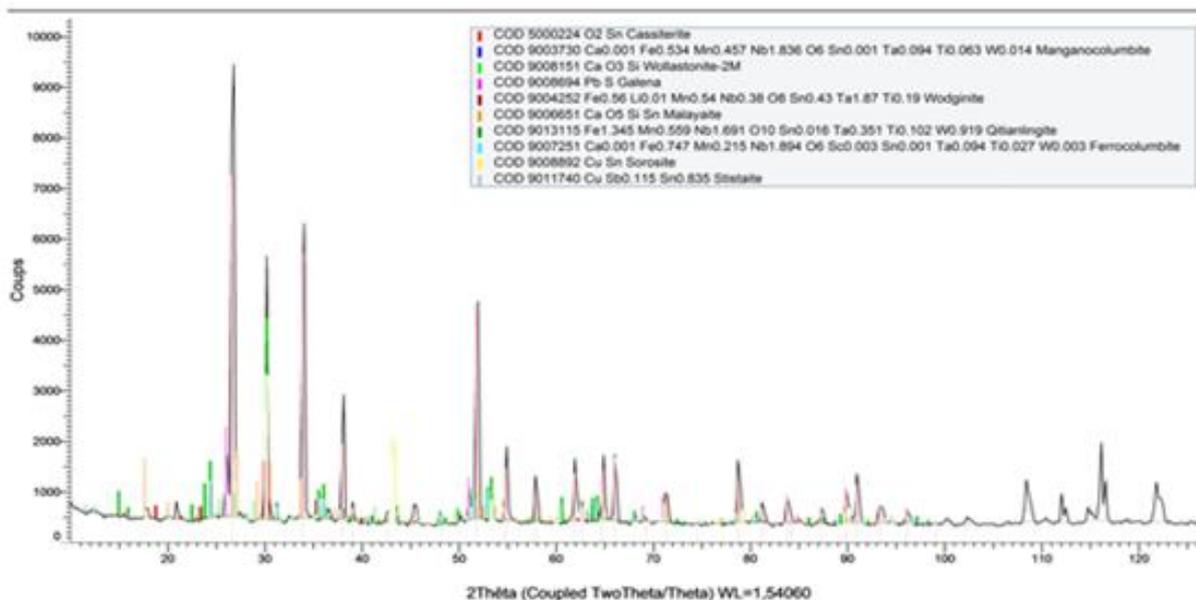


Figure 2. DRX mineralogical analysis of the sample

3.2. Ore smelting and blending of fluxes

3.2.1. Effect of NaOH/KOH mass ratio on the dissolution of elements

The test conditions were set at 1/2 the sample/(NaOH + KOH) ratio, melting temperature of 500°C, melting time of 60 minutes, 100 ml of distilled water brought to 40°C for leaching for 60 minutes. Figure 3 shows the effect of the amount of sodium hydroxide in the flux mixture (NaOH+KOH) on the leaching of the elements (Sn, Si and Fe). The best leach efficiencies for tin and silicon were observed between 20 and 50% NaOH in the mixture while for iron, between 10 and 80% NaOH. As KOH is a little more expensive than

NaOH, in this work the mass percentage of 50% was chosen for a better leaching yield of tin of 66.29% and those of Si and Fe are 49.47% and 21.51% respectively.

In molar percentage, this results in 58% NaOH and 42% KOH. A previous study also showed, without the sample, a slight predominance of 51% molar percent NaOH over 41% KOH (Eluard, 1970); therefore, the presence of cassiterite ore in this study required a 7% molar increase in NaOH.

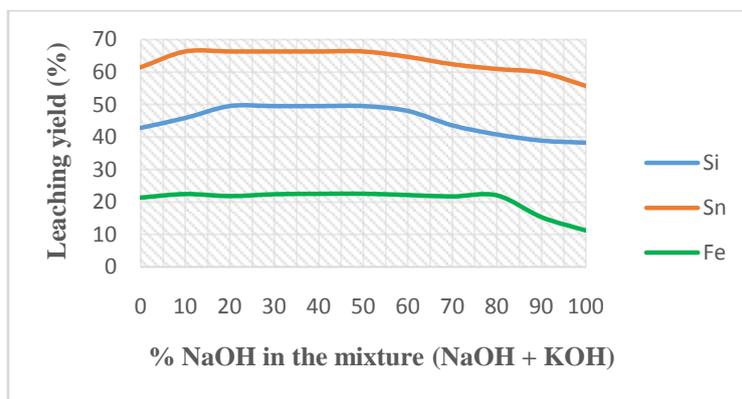


Figure 3: Effect of NaOH/KOH ratio on element dissolution

3.2.2. Effect of the amount of the flux mixture on leaching

The sample/(NaOH+KOH) ratio being variable, the other conditions were maintained for melting and leaching. As seen in Figure 4, as the sample/(NaOH+KOH) mass ratio decreased from 1/1 to 1/5, the tin leaching yield increased from 52.26 to 91.45%, respectively, beyond this range the yield remained almost constant; hence the 1/5 ratio was maintained throughout the remainder of the smelting tests. This finding showed that a high amount of mixing of fluxes in the smelting process with the cassiterite ore favoured the dissolution of tin. The quantity of fluxes used in this study is greater than that found by a group of researchers (Choosri, et al., 1990) who had worked on the cassiterite concentrate under conditions of -300 particle size and a sample/NaOH ratio of 1/3 at 700°C. The mixture of NaOH with KOH was the basis for this improvement, although the melting temperature for this test was 500°C. The silicon leaching yield follows the pattern of tin although its optimum gives a value of 68.31% at the 1/6 ratio. For iron, the reasons remain plausible.

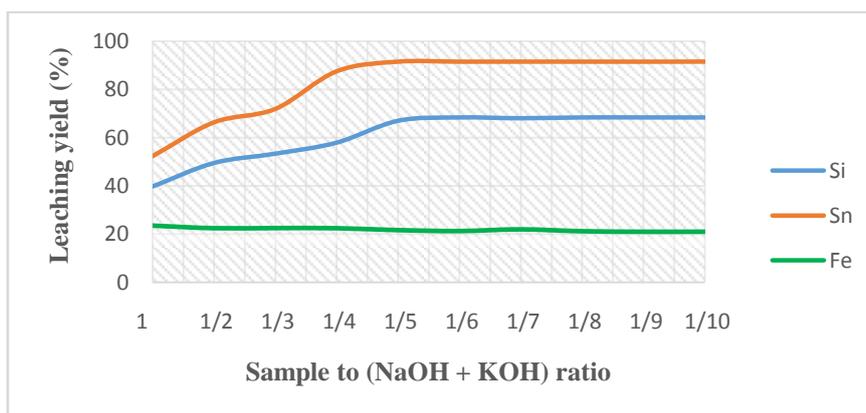
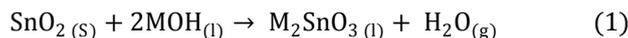


Figure 4: Influence of sample/(NaOH+KOH) ratio on element leaching

3.2.3 Influence of the melting temperature on the dissolution of the elements

In Figure 5, it was found that the tin leaching yield increases from 38.28 to 95.10% as one moves from 150 to 350°C; the range from 350 to 450°C was characterized by a constant yield; while at temperatures above 450°C there is the yield decrease. The temperature of 350°C was chosen for the following, which is very low compared to previous studies (Bunnakkha, et al., 2012; Choosri, et al., 1990). Silicon follows the same trend as tin with an optimal value of 79.21% at the same temperature. The literature on this eutectic mixture mentions the molar percentage of 51% NaOH and 49% KOH for a melting temperature, without the sample, of 170°C (Eluard, 1970); whereas here, with the ore, it has just been increased to 350°C. The presence of SnO₂ and SiO₂ in the ore would be at the basis of this temperature mutation which can be justified by the formation of alkaline stannate and orthosilicate, as reported by other researchers (Bunnakkha, et al., 2012) who relied on equations (1) and (2) :



where M represents Na or K in the melting process. The portion of Sn that has not passed into solution could be found as insoluble $\text{Na}_2\text{SnSi}_6\text{O}_{18}$ (Zhang, et al., 2019) which accentuates its presence when the temperature exceeds 450°C , according to equation (3):



This gives the justification for the decrease in the yield of Sn and Si when the temperature exceeds 450°C .

As for iron, its yield is low and decreases when the temperature increases, which can be justified by the presence of the following species Fe_3O_4 , FeO and Fe , insoluble in water, found from the reactions (5), (6), (7) and (8) of $\text{SnO}(\text{s})$, found by equation (4), with iron oxides:

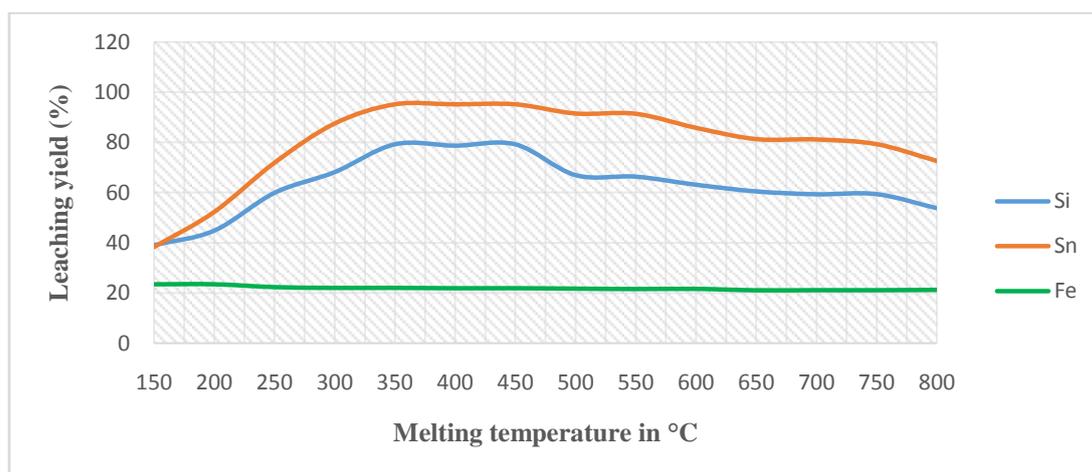
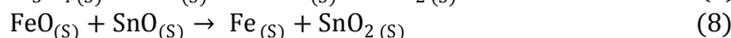
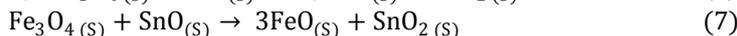
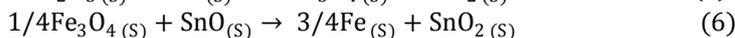
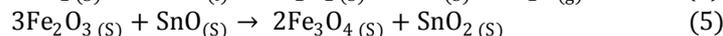
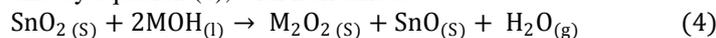


Figure 5: Influence of the melting temperature on the dissolution of the elements

3.2.4. Influence of melting time on the leaching of elements

The influence of the melting time in relation to the dissolution of Sn, Si and Fe is shown in Figure 6. The yield of Sn increased from 65.49 to 96.57% when the time increased from 15 to 90 minutes, and decreased after 120 minutes, while the yield of Si reached its optimum value of 92.24% at 120 minutes. The rate of formation of soluble alkali stannate [equation (1)] is found to be higher than that of formation of soluble alkali silicate [equation (2)] in the mixture of NaOH (50% by weight) and KOH (50% by weight) at a melting temperature of 350°C under the leaching conditions previously set. The yield of Fe was not improved but it decreased with increasing time. These results met those in the literature (Zhang, et al., 2019) which indicates that the melting time is 90 minutes and the rate of sodium stannate formation was much faster than that of sodium silicate formation in $\text{CO} - \text{CO}_2$ atmosphere.

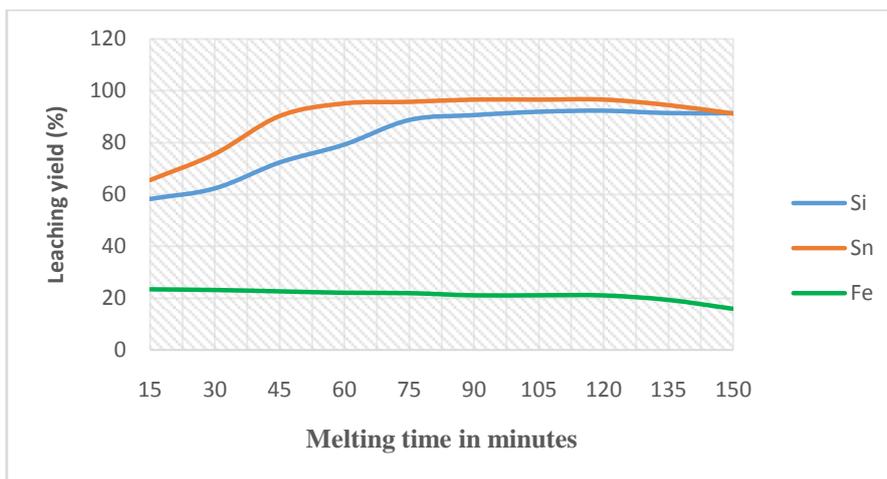


Figure 6: Influence of melting time on element dissolution

3.3. Leaching of the molten sample with the flux mixture

In this point, the 10 g leaching variables of the roasted sample were optimized by evaluating the effects of water volume, temperature and time on the leaching yields of Sn, Si and Fe.

The leach sample was prepared under melting conditions at a temperature of 350°C, a time of 90 minutes and a sample/[NaOH (50%) + KOH (50%)] mass ratio of 1/5.

As can be seen in Table 2, the Sn yield increased when the volume of leach water increased from 25 to 100 ml, giving the best yield of 96.57%, which subsequently appeared to maintain its value up to 150 ml. For Si and Fe, the best yields of 92.12% and 23.11% respectively were observed at 125 ml.

Still in Table 2, the use of 100 ml of water for leaching showed that Sn passes into solution at 96.58% at room temperature (25°C); the increase in this temperature did not show its influence up to 45°C. For Si, the increase in temperature increases its leaching efficiency up to 92.58% at 45°C. On the other hand, the increase in temperature did not explain the Fe yield.

In 100 ml of water and at room temperature, 30 minutes were sufficient to leach 96.59% Sn, 89.98% Si and 21.49% Fe, as shown in Table 2.

Table 2. Evolution of leaching yields as a function of water volume, temperature and time

Test	V(ml) water	T(°C)	Time (min)	Yield (%)			pH of leachate
				Sn	Si	Fe	
1	25	40	60	57,23	47,55	19,45	9,7
2	50			76,31	59,42	18,84	
3	75			92,18	82,05	20,48	
4	100			96,57	90,54	21,05	
5	125			96,55	92,12	23,11	
6	150			96,57	92,03	23,09	
7	100	25	60	96,58	90,45	21,56	9,7
8		30		96,57	90,48	22,52	
9		35		96,56	90,51	22,49	
10		40		96,57	90,54	21,05	
11		45		96,58	92,58	22,54	
12	100	25	20	95,72	89,76	21,33	9,7
13			30	96,59	89,98	21,42	
14			40	96,58	90,45	21,59	
15			50	96,6	91,27	22,75	
16			60	96,58	90,45	21,56	

Based on these results, it was found that the yield of tin (96.59%) found under the conditions of this study is higher than those found by Zhang et al (2019), Zhang et al (2014) and Bunnakkha and Jarupisittorn (2012) although they had used higher melting temperatures than those used here. The reasons for this are manifold, i.e., in this study, a sample with a high Sn content and a very low SiO₂/SnO₂ ratio was worked with an alkaline eutectic mixture whose theoretical melting temperature was initially about 170°C (Eluard, 1970).

It was also found that the leaching solution had a pH of 9.7 for an Sn yield of 96.59% where the species Sn(OH)₆²⁻, Sn(OH)₅⁻, HSiO₃⁻ and SiO₃²⁻ are likely to be found, according to the literature consulted (Zhang, et al., 2019).

3.4. Behaviour of tin species with respect to pH

To vary the pH of the leach solution, two solutions were used: HNO₃ 2M to decrease the pH and NaOH 1M to increase it.

As shown in Figure 7, a decrease in tin content was observed in the pH range of 1 and 2 and the initial content was again found at pH 9 to 13 with almost no change in the value. This finding reinforces the position of believing in the existence of the species Sn(OH)₆²⁻ and Sn(OH)₅⁻ at pH = 9.7. These results have met those found by other researchers (Angadi, et al., 2015; Zhang, et al., 2019) who had fixed the forms of tin species according to the pH ranges i.e. at pH < 2, we have the positively charged species [Sn⁴⁺, Sn(OH)³⁺, Sn(OH)₂²⁺, Sn(OH)₃⁺], at pH between 2 and 7.5, tin precipitates as Sn(OH)₄; for values between 7.5 and 9.5, we have the species Sn(OH)₅⁻ and at pH > 9.5, we note the presence of two species in which Sn(OH)₆²⁻ predominates over Sn(OH)₅⁻.

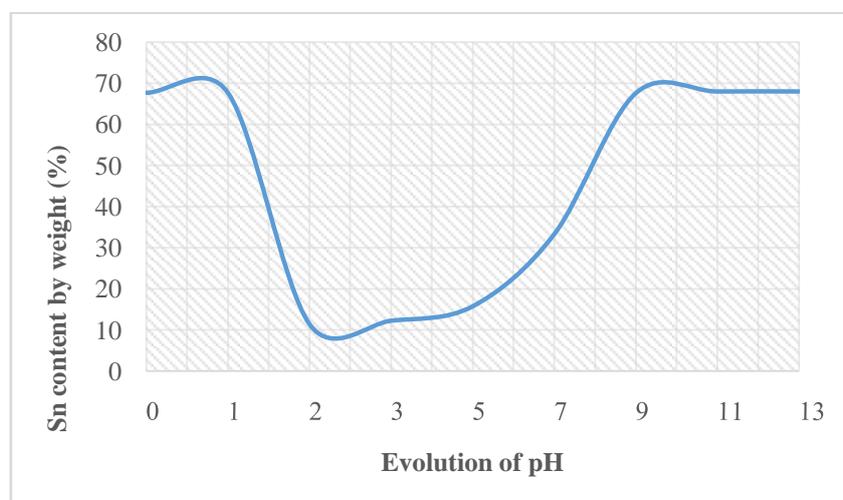


Figure 7: Influence of pH evolution on the Sn content in the solution

IV. Conclusion

In this study, tin was extracted from cassiterite ore containing 68.58% Sn. This ore was smelted with the mixture of NaOH and KOH before being leached into distilled water. After several tests, the results were concluded as follows:

- the eutectic mixture was prepared with equal mass proportions of fluxes, i.e. 50% by weight for each of NaOH and KOH ;
- the ore was reduced to a grain size < 75µm before being mixed with the eutectic mixture at a ratio of 1/5 ore/(NaOH+KOH) and melted at 350°C for 90 minutes to form soluble M₂SnO_{3 (S)} (M = Na or K) and also M₈SnSi₆O_{18 (S)} insoluble in water ;
- 10 g of the roasted sample were leached in 100 ml of water for 30 minutes at room temperature (25°C) to give a leaching yield of 96.59% tin; the leached solution was characterized by a pH of 9.7 showing the presence of the species Sn(OH)₆²⁻ and Sn(OH)₅⁻ ;
- the tin species changed their forms when the pH was varied, namely, Sn⁴⁺, Sn(OH)³⁺, Sn(OH)₂²⁺, Sn(OH)₃⁺ at pH < 2 ; Sn(OH)₄ to 2 ≤ pH ≤ 7.5; Sn(OH)₅⁻ to 7.5 ≤ pH ≤ 9.5 and Sn(OH)₆²⁻ predominates at [Sn(OH)₅⁻ at pH > 9.5.

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