Role of the reducing agent in tungsten extraction by chlorination with chlorine from an ore enriched by physical means

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Carlos J. Menéndez[1,3]
https://orcid.org/0000-0001-5112-292X
Eduardo L. Tavani[2,4]
https://orcid.org/0000-0003-4145-7800

[1]Facultad de Química, Bioquímica y Farmacia,
Universidad Nacional de San Luis (UNSL)
Chacabuco 915, (D5700BWS) San Luis - Argentina.

[2]Centro de Tecnología de Recursos Minerales y Cerámica (CETMIC), Comisión de Investigaciones Científicas de la Provincia de Buenos Aires (CIC)
Camino Centenario y 506, (B1897ZCA) M.B. Gonnet - Buenos Aires - Argentina.

E-mails: [3]cmenend@unsl.edu.ar,
[4]etavani@cetmic.unlp.edu.ar

Abstract

The effect of three reducing agents (sulphur dioxide, pyrite and carbon) on tungsten extraction from a scheelite-wolframite concentrate with chlorine gas was assessed. A low-grade ore (0.9% w/w WO_3) was collected in the San Martín department, San Luis Province, Argentina, and subsequently enriched by physical means (65.73% w/w WO_3). The minerals identified and their reactivities with chlorine were: scheelite (reactive), wolframite (reactive), pyrite (reactive), quartz (inert) and feldspars (inert). The metal recovered as WO_2Cl_2, with the different reagent combinations, was in increasing order: $Cl_2 + N_2 < Cl_2 + SO_2 <$ pyrite $+ Cl_2 + N_2 <$ pyrite $+Cl_2 + SO_2 <$ carbon $+ Cl_2 + N_2$. It was proved that, according to its content, the pyrite initially present in the ore improves chlorination performance. At the same time, the non-volatile reaction products formed – $CaCl_2$ and/or $CaSO_4$ – and the manner of removing the nascent (desorbed) oxygen change depending on the reducing agent tested.

Keywords: sulphur dioxide, pyrite, carbon, scheelite-wolframite concentrate, free energy change.

1. Introduction

Refractory metals have a high melting point (around 2000 °C) and significant chemical resistance (Lipetzky, 2002; Schade *et al*., 2015). The operating conditions required to remove the combined oxygen (Me–O) from its bearing minerals are very difficult to obtain. A suitable technique for such a purpose is chlorination (Jena *et al*., 1999, Menéndez *et al*., 1999; Menéndez *et al*., 2007; Brocchi & Moura, 2008; Kanari *et al*., 2010; De Mico *et al*., 2011; Fouga *et al*., 2012, Brocchi *et al*., 2013; Anderson & Mishra, 2015). The halides produced generally melt at low temperature and are volatile, which facilitates their corresponding purification (Lassner & Schubert, 1999). This is an appreciable difference compared with solvent extraction, a stage usually employed to achieve this purpose and whose implementation is certainly complex (Lassner & Schubert, 1999; Vera & Braga, 2020).

The chlorination mechanism was the focus of a widespread scientific debate. At present, acceptable consensus has been reached that chlorine is initially adsorbed on the surface of the solid (Tench & Kibblewhite, 1972; Kibblewhite & Tench, 1974; Szepvölgyi *et al*., 1988; Andrade Gamboa & Pasquevich, 1992; Jena *et al*., 1999). This association was attributed to the energy excess of oxygen atoms and to the vacancies on the more external crystalline planes (Andrade Gamboa & Pasquevich, 1992). The replacement of the above-mentioned element is carried out by means of a solid-gas reaction with electron transfer ($2\ O_{lattice} + 2\ Cl_2 \rightarrow 4\ Cl^- + O_2\uparrow$). All of these stages improve their efficiency in the presence of substances capable of interacting with the nascent oxygen.

Several commercial goods are manufactured by chlorination. It is considered that its most recognized process is, from an economic standpoint, the titanium extraction from rutile. Likewise, the development of new possible uses should be highlighted (Pozan & Kambur, 2014). Therefore this route could be appropriate to prepare the precursor tungsten hexachloride (WCl_6) when the aim is to obtain tungsten carbide (WC) with a very fine particle size (Lassner & Schubert, 1999; Ma & Du, 2008; Zak Fang *et al*., 2009). The interest in this material is because its properties make it fit for a wide range of industrial applications. However, studies on the synthesis of such a halide and its intermediate compounds are very limited. With this idea in mind, seeking further clarifications on the physical and chemical behaviour of the W–Cl_2 system was regarded as a matter of interest (Nolasco *et al.*, 1991; Menéndez *et al.*, 1999; Menéndez *et al.*, 2007; De Mico *et al.*, 2011; Fouga *et al.*, 2012).

There are two main tungsten minerals: scheelite ($CaWO_4$) and wolframite ($Fe_xMn_{1-x}WO_4$), but they differ from each other by their crystalline structure as well as by their chemical composition. The latter is a solid solution whose end members of the series are ferberite ($0.8 < x < 1.0$) and hübnerite ($0 < x < 0.2$) (Lassner & Schubert, 1999). In Argentina, abundant deposits of scheelite associated with wolframite have been found. These natural resources contain variable proportions of both constituents and are irregularly distributed over the surface of each grain bearing the refractory metal (Angelelli, 1984). Impurities are initially removed by grinding, followed by physical treatments, resulting in a scheelite-wolframite concentrate (SWC) suitable to be utilized in extractive metallurgy.

The literature accurately describes the basic and applied technological issues (Menéndez *et al.*, 1999; Menéndez *et al.*, 2007). As a proven fact, it is noted that SWC chlorination with Cl_2 and SO_2 leads to the formation of $CaSO_4$. The effect caused by this salt, equivalent to a barrier, is characterized by hindering the diffusion – spherical symmetry – both to and from the reactive interface (Menéndez *et al.*, 1999). The replacement of the reducing agent represents an alternative way of modifying the reaction mechanism. On this basis, the aim of our work was to compare the yield of sulphur dioxide, pyrite and carbon in tungsten extraction from a SWC with chlorine.

2. Materials and methods

2.1 Ore enrichment

A low-grade ore (0.9% w/w WO_3) was collected in the San Martín department, San Luis Province, Argentina. The useful components were released when the particle size was reduced so that at least 85% of the total was in the range of 180-300 µm. Then, the enrichment was performed by gravity separation using jig and shaking table. The concentrate particles were classified according to the American Standard Test Sieve Series designated by their opening size in microns.

2.2 Reactor description

The chlorination equipment used was composed of a vertical reactor with a static bed and upward flow. It also had a gas premixing chamber and a collector where substances with a melting point above 150 °C solidified. Chlorine, sulphur dioxide and nitrogen were supplied from three separate cylinders, each one with a control valve and flowmeter. The sample was placed within the reactor on a ceramic fibre (Kaowool) to favour the homogenization and heating of the $Cl_2 + N_2/SO_2$, employing 3 g per test. Smaller weights made the results erratic, since it is difficult to keep the proportion of the constituents constant. There were no operational complications concerning the thickness (~3 mm) of the resulting bed or particle size (-300 µm +53 µm). The gases discharged ($Cl_2 + SO_2 + SO_3$) at the reactor exit were bubbled in a concentrated $Ba(OH)_2$ solution. An identical flow of 500 mL min^{-1} was employed in every test to maintain the dynamic conditions that regulate the reactor performance. This rate prevented fluidization and the appearance of channels in the particulate material.

The temperature was attained with an electric furnace, which could be regulated to obtain the desired value ±2°C. A 500 mL min^{-1} N_2 flow was circulated until reaching 750 °C. At this moment, nitrogen was replaced by 300 mL min^{-1} of Cl_2 + 200 mL min-1 of N_2 or SO_2. After 10 min, nitrogen was passed again while the furnace was turned off and cooled down to achieve the room temperature. Reaction temperature was measured by a thermocouple and displayed on a digital thermometer.

2.3 Experimental methodology

Chlorinations were done at 750 °C with 300 mL min^{-1} of Cl_2 and 200 mL min^{-1} of N_2 or SO_2, depending on the strategy applied in the five systems studied: (1) SWC + Cl_2 + N_2, (2) SWC + Cl_2 + SO_2, (3) SWC + 25% w/w of pyrite + Cl_2 + N_2, (4) SWC + 25% w/w of pyrite + Cl_2 + SO_2, and (5) SWC + 12.5% w/w of carbon + Cl_2 + N_2. Minerals and reaction products were identified by chemical analysis (CA), X-ray diffraction (XRD), scanning electron microscopy (SEM) and measurement of the surface chemical composition by energy dispersive X-ray spectroscopy (EDS). Tungsten extraction (α) was determined by CA of the chlorination residue (fraction that remained unattached), then a new SWC aliquot was used in the following run. The α values reported were the average of two duplicate chlorinations, the difference between them was never higher than 3%.

The analytical techniques used were volumetry (Fe, Ca, Mn, Al), gravimetry (W, Si, S) and atomic emission (AE) with a Jarrell Ash equipment for the alkaline metals (Na, K). The XRD study was carried out with a Philips 3 kW X'Pert diffractometer, Cu Kα radiation and Ni filter. SEM-EDS observations were performed with a Leo 1450 VP instrument and an EDAX Genesis 2000 spectrometer. In order to find out the feasibility of a proposed reaction, the free energy change (ΔG) was calculated (Menéndez *et al.*, 2007; Brocchi *et al.*, 2013) on the basis of diagrams reported in the literature (Rosenqvist, 1987; Um & Lee, 1993; Fouga *et al.*, 2012).

3. Results and discussion

3.1 Mineralogical and chemical characterization of the ore

The particle size distribution, CA and semi-quantitative mineralogical composition of the SWC are shown in Tables 1, 2 and 3, respectively. The diffraction pattern of the concentrate produced in this study allowed the identification of scheelite, wolframite and quartz (Figure 1). It was established that the two tungsten-bearing species ($CaWO_4$ and $Fe_xMn_{1-x}WO_4$) are closely associated, which makes their separation by physical means almost impossible. Pyrite is an impurity that participates in successive exothermic reactions. From 600 °C and according to Eq. (1), it decomposes into sulphur, an element that solidifies before leaving the collector, and pyrrhotite (FeS) that remains in the sample bed (Menéndez *et al.*, 1999). When ore purification is done manually under a binocular microscope, scheelite (74.90% WO_3; 18.10% CaO; 1.09% FeO; 0.04% MnO; 3.41% SiO_2; 0.01% S) and wolframite (67.73% WO_3; 21.47% FeO; 1.19% MnO; 0.24% CaO; 6.90% SiO_2; 0.01% S) without FeS_2 are obtained. This is a fundamental difference with the SWC that allows us to prove our point of view.

Table 1 – Particle size distribution of the SWC.

Sieve designation in µm*	% w/w
-300 µm +250 µm	22.90
-250 µm +212 µm	35.50
-212 µm +180 µm	28.80
-180 µm +150 µm	8.10
-150 µm +90 µm	4.60
-90 µm +53 µm	0.10

* American Standard Test Sieve Series

Table 2 – Chemical analysis of the SWC.

	WO_3	FeO	MnO	CaO	Al_2O_3	Na_2O	K_2O	SiO_2	S	LOI*
(% w/w)	65.73	12.55	0.79	10.48	0.86	0.46	0.12	3.70	2.42	3.10

* Loss on ignition (1100°C)

3.2 SWC+Cl_2+N_2

The oxidation of FeS_2 generates noticeable heat release (Rosenqvist, 1987; Menéndez *et al.*, 1999; Weiler & Schneider, 2019). However, volatilization of S_2 (Eq. (1)) while heating the reactor – in the presence of an inert atmosphere – prevents a higher temperature increase (Eqs. (2) and (3)). According to these antecedents, tests were started at a slightly lower value than the one desired and the furnace power was immediately increased, a methodology that compensates for pyrite depletion. The average of the maximum and final records, provided that the difference was less than 7 °C, was taken as the run temperature. With the highest thermal gradient, a partial sintering of the sample was observed, changing its porosity and the efficacy of this technique. Both issues were minimized at 750 °C.

$$2\ FeS_2\ (s) \rightarrow 2\ FeS\ (s) + S_2\ (g) \qquad \Delta G_{750°C} = \sim -20\ kJ \qquad (1)$$

$$FeS\ (s) + 1.5\ O_2\ (g) \rightarrow FeO\ (s) + SO_2\ (g) \qquad \Delta_{G750°C} = \sim -390\ kJ \qquad (2)$$

$$S_2\ (g) + 2\ O_2\ (g) \rightarrow 2\ SO_2\ (g) \qquad \Delta_{G750°C} = \sim -580\ kJ \qquad (3)$$

The volume (weight) of Cl_2 for 3 g of SWC was settled by stoichiometry (Eqs. (4) and (5)): ~420 mL NTP (1.3 g). If it is considered that the total flow should not exceed 500 mL min^{-1}, an amount a little higher than half of the maximum value – 300 mL min^{-1} – ensures the supply of the gas in relatively short times (<1.5 min). With this procedure, a low yield would not be attributable to insufficient reagent. The operational variables selected (3 g of SWC, 750 °C, 300 mL min^{-1} of Cl_2 + 200 mL min^{-1} of N_2) showed that the extraction of tungsten had minor variations from 5 min. Thus, 10 min is more than sufficient to complete the chemical attack of the minerals.

Table 3 – Semi-quantitative mineralogical composition of the SWC.

Mineral	% w/w
Scheelite (CA, XRD, SEM-EDX)	50-60
Wolframite (CA, XRD, SEM-EDX)	25-35
Feldspars (CA, SEM-EDX)	4-7
Pyrite (CA, SEM-EDX)	2-6
Quartz (CA, XRD, SEM-EDX)	2-4

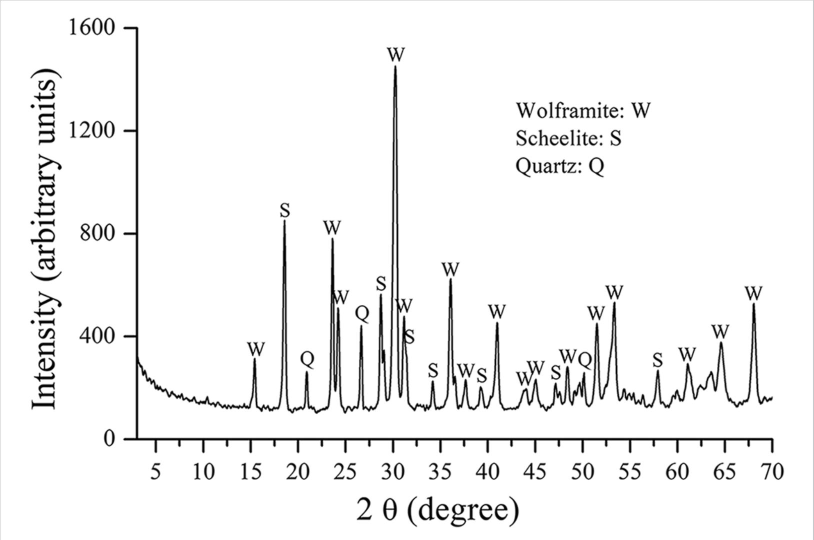

Figure 1 – Diffraction pattern of a representative sample of the SWC.

Four substances solidified in the collector (WO_2Cl_2, S_2, $FeCl_2$, $FeCl_3$), whereas three ($CaCl_2$, $CaSO_4$, FeS) remained on the mineral unreacted. This heterogeneity of the reaction products prevented the determination of the conversion degree by weight loss. Figure 2 exhibits the tungsten extraction vs. the reducing agent employed, the lowest was $\alpha = 40\%$ and corresponds to $Cl_2 + N_2$ (Eqs. (4) and (5)). Its positive ΔG (Um & Lee, 1993; Fouga *et al.*, 2012) would suggest that these are thermodynamically unfavourable processes, but the results indicate otherwise. An argument that explains such a contradiction is that when the volatile reaction products are removed, their formation continues (Le Châtelier's principle) (Fouga *et al.*, 2012). Besides, it was confirmed that the tungsten halide (WO_2Cl_2) was the same for both species bearing the refractory metal. The displacement of the O_2 released from each reactive interface is produced by the drag of Cl_2 and N_2.

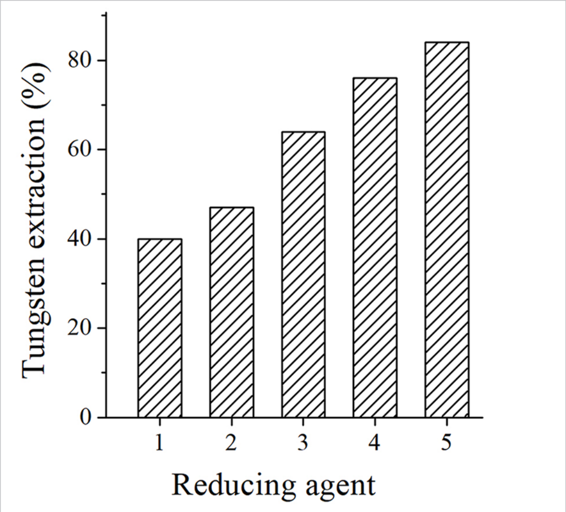

Figure 2 – Tungsten extraction from 3 g SWC (750 °C, 10 min, 300 mL min^{-1} Cl_2), as a function of the aggregate-reducing agent: (1) 200 mL min^{-1} N_2, (2) 200 mL min^{-1} SO_2, (3) 25.0% w/w of pyrite + 200 mL min^{-1} N_2, (4) 25.0% w/w of pyrite + 200 mL min^{-1} SO_2, and (5) 12.5% w/w of carbon + 200 mL min^{-1} N_2.

Calcium chloride was obtained from scheelite (calcium oxide) + Cl_2 + N_2 (Eqs. (4) and (6)). This substance melts at 782 °C (Hammond, 1981) and its presence in the residue was recognized by SEM-EDX microanalysis. The calcium:chlorine ratio measured was ~39%:~61%; so, dividing such percentages by the respective atomic weights resulted in: ~39/40: ~61/35.5 = ~0.97: ~1.72 = 1:~1.77 ($CaCl_{1.77}$). With respect to the iron contained in wolframite, it was assumed that it participated in the synthesis of $FeCl_2$ (Eqs. (5) and (7)). However, this ferrous salt is almost completely converted into $FeCl_3$ by the oxidizing action of chlorine (Nagata and Bolsaitis, 1987). A spontaneous thermal effect, which occurs in the section of the collector where the temperature is ~300°C, causes part of the ferric chloride to be transformed once again into ferrous chloride (Menéndez *et al.*, 1999; Menéndez *et al.*, 2007). The coexistence of the mentioned cations was verified by chemical analysis. Iron(II) was titrated with potassium dichromate and diphenylaminosulfonic acid, while for the determination of total iron the trivalent state was previously reduced in acidic medium with Al powder.

The $Fe_2(SO_4)_3$ decomposes at 480 °C (Hammond, 1981), a temperature lower than the one used in the tests; hence, this substance was not taken into consideration in the discussion. Manganese content is low and when combined with Cl_2, it produces $MnCl_2$. Under our operating conditions, this compound is in a liquid state and flows by gravity through the ceramic fibre (melting point = 650°C) (Hammond, 1981). In previous articles, it was demonstrated that the kinetics of several manganese-bearing species remained unaltered (Fouga *et al*., 2012; Menéndez *et al*., 2007). For this reason, its analysis was also omitted.

$$CaWO_4\ (s) + 2\ Cl_2\ (g) \rightarrow WO_2Cl_2\ (g) + CaCl_2\ (s) + O_2\ (g) \qquad \Delta G_{750°C} = \sim +85\ kJ \qquad (4)$$

$$Fe_xMn_{1\text{-}x}WO_4\ (s) + 2\ Cl_2\ (g) \rightarrow WO_2Cl_2\ (g) + x\ FeCl_2\ (g) + (1\text{-}x)\ MnCl_2\ (l) + O_2\ (g) \qquad \Delta G_{750°C} = \sim +50\ kJ \qquad (5)$$

$$CaO\ (s) + Cl_2\ (g) \rightarrow CaCl_2\ (g) + 0.5\ O_2\ (g) \qquad \Delta G_{750°C} = \sim -115\ kJ \qquad (6)$$

$$FeO\ (s) + Cl_2\ (g) \rightarrow FeCl_2\ (g) + 0.5\ O_2\ (g) \qquad \Delta G_{750°C} = \sim -25\ kJ \qquad (7)$$

3.3 SWC+Cl_2+SO_2

The stoichiometric calculation was repeated to determine the weight (volume) of SO_2 (Eqs. (4), (5) and (8)): 420 mL NTP (1.2 g). The N_2 (200 mL min^{-1}) is replaced by the reducing agent (200 mL min^{-1}) and after 2 min, the required amount of this reagent is achieved. With Cl_2 + SO_2, the O_2 formed from scheelite (Eq. (4)) and wolframite (Eq. (5)) is eliminated in two stages, drag, as in the case of Cl_2 + N_2, and chemical reaction (Eq. (8)). The resulting trioxide is combined with the calcium oxide of scheelite (Eq. (9)), the surface composition (SEM-EDX) of the latest salt being: ~26% calcium, ~22% sulphur and ~52% oxygen ($CaS_{1.1}O_{5.0}$). Any of the non-volatile products ($CaCl_2$ or $CaSO_4$) delays the release of molecular oxygen and prevents the passage of Cl_2 – and, if applicable, of SO_3 – towards the surface sites that are still active.

The possible sequence to obtain calcium chloride would require that the halogen be retained on the external crystalline planes and displace the lattice oxygen (Eq. (6)). If the product is calcium sulphate (Eq. (9)), three consecutive stages rather than two are required, as was indicated. It begins with the oxidation of SO_2 to SO_3 (Eq. (8)), then, this molecule competes with a smaller one (Cl_2) to be adsorbed and, subsequently, it combines with CaO. Comparison of the $\Delta G_{750°C}$ for $CaCl_2$ (Eq. (6)) and $CaSO_4$ (Eq. (9)) suggests that the second salt prevails, even though its reaction mechanism seems to be more complex.

Another issue of interest was to know how the two minerals without pyrite respond when they are chlorinated separately (3 g, 300 mL min^{-1} of Cl_2 + 200 mL min^{-1} of SO_2, 750 °C, 10 min). It was established that the reactivity of wolframite was much higher than that of scheelite: 41% and 20%, respectively. Cl_2 consumption was significantly reduced in the presence of SO_2, and tungsten extraction increased from 40% to 47% (Eqs. (4), (5), (8) and (9)). A new test at 750 °C was done with 500 mL min^{-1} of Cl_2 and after 10 min, α was ~10% lower. Consistent with these results, the most plausible explanation is that the SO_2 participates in the removal of the O_2 released from the solid-gas interface.

$$SO_2\ (g) + 0.5\ O_2\ (g) \rightarrow SO_3\ (g) \qquad \Delta G_{750°C} = \sim -10\ kJ \qquad (8)$$

$$CaO\ (s) + SO_3\ (g) \rightarrow CaSO_4\ (s) \qquad \Delta G_{750°C} = \sim -230\ kJ \qquad (9)$$

3.4 SWC+pyrite+ Cl_2+N_2

The oxidation of FeS (Eq. (2) = -390 kJ) is much more favourable than that of SO_2 (Eq. (8) = -10 kJ) and it would justify the higher tungsten extraction with pyrite, α = 64%. The reducing agent (particle size = 180-300 µm) was mixed with the concentrate manually. Figure 2 suggests that the ΔG values for each mineral in Eqs. (4) and (5) do not correspond to the scheelite-wolframite concentrate. Pyrite plays an extremely active role in chlorination: it is an impurity that substantially affects the behaviour of the ore.

To confirm this trend, a sample was prepared with the same percentages of scheelite, wolframite, quartz and feldspars as those in the concentrate. Such mixture (SWM) was divided into four parts, and different amounts of FeS_2 (0, 10, 20, 25% w/w) were added to each of them. Next, these aliquots were chlorinated with 300 mL min^{-1} of Cl_2 + 200 mL min^{-1} of SO_2 at 750 °C, for 10 min. The α values achieved with such methodology are shown in Figure 3 and its performance would corroborate our hypothesis. This effect provides an alternative viewpoint to the one formulated in Section 3.2 (Le Châtelier's principle) to explain that, despite the positive values of ΔG > 0 given in Eqs. (4) and (5), significant tungsten extractions were obtained. The downside is that it greatly increases the use of chlorine, and the by-product has little commercial value ($FeCl_2$/$FeCl_3$).

3.5 SWC+pyrite+Cl_2+SO_2

During the SWC chlorination with FeS_2 and SO_2, $CaSO_4$ was not detected in the residue (Eq. (9)), and at the same time it was observed that α increased to 76% (Figure 2). By means of a simple calculation, it was established that 25% w/w of FeS_2 (0.75 g) exceeds by ~10% the required percentage of such sulphide (Eqs. (1) – (2)) to combine with all the O_2 feasible to be released from SWC (Eqs. (4) – (5)). If to this amount we add SO_2, there is an excess of reducing agents that would favour the shift of the aforementioned chlorination reactions to the right. A test with 33% w/w FeS_2 (300 mL min^{-1} of Cl_2 + 200 mL min^{-1} of SO_2, 750 ° C, 10 min) improved tungsten extraction (81%), a fact that certainly corroborates the proposed mechanism. The variation caused by working with pyrite and sulphur dioxide simultaneously would be explained by the law of mass action.

The same α (76%) was obtained for the chlorination of SWC, maintaining the flow of reactive gases (300 mL min^{-1} of Cl_2 + 200 mL min^{-1} of SO_2) but extending its duration to 60 min, a system variable that can be compared to performing the process with 25% w/w of pyrite. The above shows that it is possible to reach a similar result applying different strategies, which indicates the multiplicity of options offered by this technique.

SEM micrographs of three chlorination residues performed under different operating conditions are displayed in Figure 4: (a) low – $Cl_2 + N_2$, (b) medium – $FeS_2 + Cl_2 + N_2$, and (c) high – $FeS_2 + Cl_2 + SO_2$. These images show how the morphology and size of the residual grains change with each chemical attack. Obviously, the resulting smaller particle size also contributes to improving the surface adsorption of Cl_2.

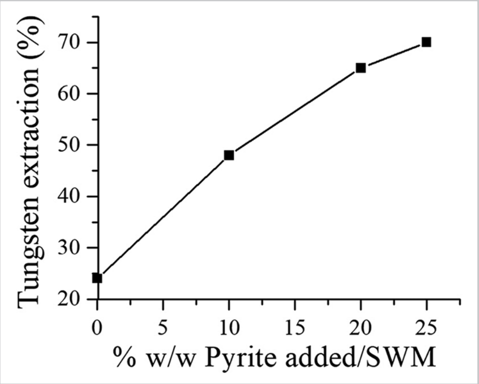

Figure 3 – Tungsten extraction versus % of pyrite added to the SWM.

3.6 SWC+C+Cl_2+N_2

Nolasco *et al.* (1991) proved that carbon had a very high yield when it was used in scheelite chlorination (1.0 g of reducing agent per 10.0 g of the mineral). The $CaCl_2$ is the barrier that prevents the passage of gaseous substances to and from the reaction interface. Carbon (graphite) combines with oxygen to form two oxides (Eqs. (10) and (11)) (Brocchi *et al.*, 2013). In atmospheres where oxygen pressure is insufficient and the temperature is above 700°C, as in our case, conversion to carbon monoxide predominates (Eq. (10)) (Rosenqvist, 1987; Anderson & Mishra, 2015). The free energy change of this reaction (Eq. (10)) per mol of O_2 removed is higher than that of FeS (Eq. (2)) (Rosenqvist, 1987) and the difference between their values would explain the observed behaviour.

Other authors mentioned a possible catalytic effect of the carbon surface that would cause the Cl_2 dissociation into radical ($Cl_2 \rightarrow 2\ Cl^*$) or the formation of intermediate compounds: carbonyl dichloride ($COCl_2$), carbon tetrachloride (CCl_4) and metal carbonyl (MeCO) (Barin & Schuler, 1980; Nolasco *et al.*, 1991; Evans *et al.*, 1998; Jena *et al.*, 1999; Ojeda *et al.*, 2003; Manukyan & Martirosyan, 2003; González *et al.*, 2004; Anderson & Mishra, 2015). The existence of more active compounds than the original element was proposed based on experimental data and thermodynamic computation, but none of such species was detected when the carbochlorination reactions occurred.

$$2\ C\ (s) + O_2\ (g) \rightarrow 2\ CO\ (g) \qquad \Delta G_{750°C} = \sim -410\ kJ \qquad (10)$$

$$C\ (s) + O_2\ (g) \rightarrow CO_2\ (g) \qquad \Delta G_{750°C} = \sim -395\ kJ \qquad (11)$$

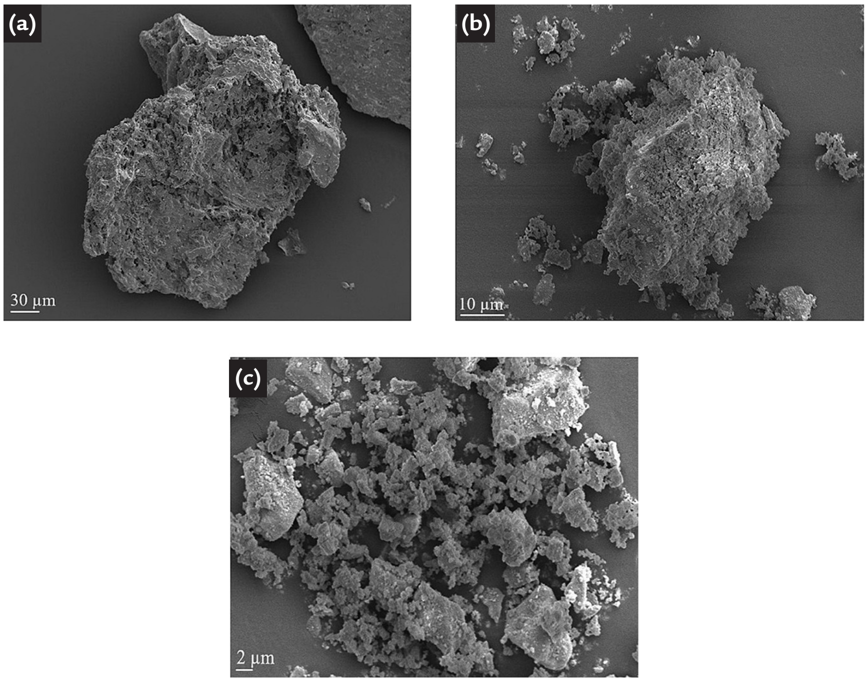

Figure 4 – SEM micrographs of residues that come from three different tungsten extractions: (a) low – $Cl_2 + N_2$, (b) medium – $FeS_2 + Cl_2 + N_2$, and (c) high – $FeS_2 + Cl_2 + SO_2$.

The advisability of grinding the carbon to a size below 212 µm, but not beyond 106 µm, and mixing it manually with the concentrate was established from exploratory tests (Nolasco *et al.*, 1991). The opinion on this methodology is not unanimous; there are those who argue that such an intimate contact between the reactive solid phases is not necessary (Barin & Schuler, 1980; Jena *et al.*, 1999). Under operating conditions arbitrarily chosen with the sole purpose of keeping them similar to the previous ones and thus having comparable records (mineral:reducing agent ratio 3.0:0.375 (g/g), 300 mL min^{-1} of Cl_2 + 200 mL min^{-1} of N_2, 10 min and 750 °C), α was 84%. Such a percentage is one of the highest reported up to now: 94% (Zhu *et al.*, 2014), 89% (Nolasco *et al.*, 1991) and 70% (Paulino *et al.*, 2012). Our results confirm that the yield of the chemical attack changed significantly depending on the reducing agent employed, and that this technology may be applied for tungsten.

4. Conclusions

It was established that the nascent oxygen removal during chlorination of a SWC with chlorine gas depends on the reducing agent used. A similar relationship was observed for the non-volatile product formed, be it $CaCl_2$ or $CaSO_4$. Either of these salts is a diffusive barrier that prevents the passage of gaseous substances to and from the surface of the mineral.

Pyrite is an impurity that is usually found in the concentrate and, due to its strong reducing power, it favours the reactivity of the refractory metal-bearing species. This effect is proportional to its content in the ore. Its main disadvantage is that it greatly increases the consumption of Cl_2.

The secondary reaction products obtained from scheelite remain in the residue ($CaCl_2$/$CaSO_4$) and those from wolframite solidify in the collector ($FeCl_2$/$FeCl_3$). The tungsten oxychloride formed from both minerals is the same (WO_2Cl_2), having removed an equal amount of oxygen in each case.

Tungsten extraction, in decreasing order, was: 84% with carbon + Cl_2 + N_2, 76% with FeS_2 + Cl_2 + SO_2, 64% with FeS_2 + Cl_2 + N_2, 47% with Cl_2 + SO_2, and 40% with Cl_2 + N_2. Carbon in combination with Cl_2 was the most efficient reducing agent to undertake the chemical attack of the mineral tested.

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