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Physicochemical characterization of the chlorination of natural wolframites with chlorine and sulphur dioxide

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Abstract

The chlorination of natural wolframites ($Mn_xFe_{1-x}WO_4$) with chlorine and sulphur dioxide was studied in a vertical reactor with a static bed and upward flow of reactive gases. Wolframite samples collected from five different deposits of Argentina were carefully purified by hand under a binocular microscope. Upgraded specimens with this methodology had a variable ratio of divalent metals ($0.06 < x < 0.84$) for similar tungsten content ($WO_3 = 72.4$–73.3%). Experimental conditions more appropriate to make chlorinations were established using the iron-rich wolframite. Under these conditions, the tungsten extraction was determined as a function of the ratio of iron(II) and manganese(II) present in each sample. Physicochemical characterization of the system involved measurement of wolframite cell dimensions, identification of reaction products formed from metallic elements (tungsten, iron and manganese) and reactivity evaluation of both divalent metals by means of thermodynamic parameters. Results obtained show that iron-rich wolframites had higher reactivity with respect to other solid solution specimens. Reaction products identified were all volatile, except manganese(II) chloride found in liquid state. Thermodynamic analysis confirmed that formation of iron oxychloride (FeOCl) as an intermediate chlorination product would be feasible, although it was not possible to observe any evidence of this reaction under experimental conditions used. Finally, it is indicated that the highest reactivity of iron-rich wolframites was attributed to the volatile nature of all their reaction products, to iron(II) oxidation easiness if compared with manganese(II) and to possible formation of iron oxychloride.

Keywords: Wolframite; Ferberite; Hübnerite; Chlorination; Tungsten

1. Introduction

Scheelite ($CaWO_4$) and wolframite ($Mn_xFe_{1-x}WO_4$) are the most abundant tungsten minerals, but they differ between them by their crystalline structure as well as by their chemical composition. From a mineralogical point of view, the generic name wolframite corresponds to species represented by the solid solution whose end-members of the series are hübnerite ($MnWO_4$) and ferberite ($FeWO_4$) (Blackburn and Dennen, 1994; Sleight, 1972).

Ores of both minerals after their upgrading are chemically processed to recover tungsten by leaching with soda in autoclave, caustic leaching in autoclave or roasting with soda and leaching. The selection of the most convenient process is performed taking into account the mineral and tungsten content of the ore. The product formed with the three processes is soluble sodium tungstate. Undesirable impurities that remain dissolved together with tungsten are removed by solvent extraction or ion exchange. In successive stages, it is possible to obtain tungstic acid (H_2WO_4) and ammonium paratungstate (APT) $[(NH_4)H_2W_{12}O_{42}]\cdot 4H_2O$. Then, APT is calcined up to its decomposition to tungsten trioxide (WO_3) or tungsten blue

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oxide (WO_{3-x}). Finally, tungsten present in such oxides is reduced to metal by hydrogen. Tungsten recovery depends on the ore characteristics and varies between 60% and 85%. The main disadvantages of alkaline routes are: large reagent consumption, high temperature to reach melting of the reagent–mineral mixture, high pressure during lixiviation in autoclave, expensive refractory materials and strict control of the temperature (Lassner and Schubert, 1999).

Tungsten market shows at present time a noticeable interest for the manufacture of APT, the most important precursor for the majority of used products, and tungsten carbide (WC). In order to attend this demand, tungsten ores are treated by means of the most convenient process to minimize costs and to assure a permanent provision of both products.

Basic aspects to recover tungsten by chlorination of scheelite and scheelite–wolframite concentrates were analyzed by Henderson et al. (1965). In this case, the chlorination was carried out with chlorine (chlorinating agent) and carbon or sulphur dioxide (reducing agents). The chlorination reaction led to formation of volatile tungsten oxychlorides and their composition depended on experimental conditions. The separation of impurities was initially made by means of non-volatile double salt formation and fractional distillation. With a new chlorination, the tungsten oxychlorides transforms to WCl_6, substance that makes it possible the purification by distillation and the metal obtention by reduction (Yih and Wang, 1979). The chlorination process offers a simpler operative way although the cost can be higher.

Chlorination reaction begins with the adsorption of chlorine on the surface of the reactive solid (Szepvölgyi et al., 1988; Réti et al., 1987; Kibblewhite and Tench, 1974; Tench and Kibblewhite, 1972). Later on, the exchange of the lattice oxygen by chlorine and the subsequent desorption of molecular oxygen into the gaseous phase are produced. The mentioned conversion of lattice oxygen to molecular oxygen and Cl^{-1} formation involve a transfer of electrons. Such transfer was explained by the energy excess of oxygen atoms placed on the crystalline surface as well as superficial vacancies (Andrade Gamboa and Pasquevich, 1992). A fast removal of released oxygen during the chlorination leads to a reaction shift to the right (higher efficiency). The reducing agent is added to be combined with this oxygen.

A previous study about chlorination of an iron-rich wolframite using chlorine and sulphur dioxide permitted to observe the relatively low manganese reactivity with respect to iron. Even when the reaction mechanism is not clear, oxygen removal from the solid oxidic phase and transport of formed chlorides affect in a direct way to tungsten recovery (Menéndez et al., 1995).

Wolframite minerals present in diverse deposits from Argentina have a ratio of divalent metals (Fe/Mn + Fe) that vary between 16% and 94% (w/w). Different chemical composition of these specimens has been conditioned by the paragenesis of their origin deposits (Angelelli, 1984; Angelelli et al., 1983). In this work, the effect of diverse factors on wolframite reactivity with chlorine in presence of sulphur dioxide was analyzed and a heterogeneous reaction to describe the system behavior was proposed. Results obtained were discussed with the support of X-ray diffraction (XRD) and scanning electron microscopy (SEM)-energy dispersive X-ray analysis (EDX).

2. Experimental

The identification of minerals and reaction products was carried out by chemical analysis, SEM–EDX and XRD. Tungsten extraction was determined by a chemical analysis of the chlorination residue. Each value reported in this work was the average of two chlorinations performed in the same way with similar reproduction.

Chemical analyses were made by titration and gravimetry. SEM tests were performed with a microscope JEOL JSM-6360LV. Superficial chemical composition was determined with a Philips 505 scanning electron microscope and EDAX microanalysis system. XRD analyses were carried out with a Philips 3 kW X'Pert equipment, using Cu Kα radiation and a nickel filter. Cell parameters were obtained by means of the Pirum program (Werner, 1969).

Five samples were chosen from diverse wolframite deposits of Argentina. Mineral species (impurities) associated to wolframite that could be identified are in agreement with the genesis of its respective deposit. Wolframites formed by vein systems (samples 1, 4 and 5) are associated mainly to sulphide (pyrite, chalcopyrite and arsenopyrite), crystalline quartz, scheelite, feldspars and micas. Principal species present in wolframites of pegmatite origin (samples 2 and 3) are crystalline quartz, feldspars, micas, scheelite and iron oxide minerals.

Impurities were carefully separated by hand under a binocular microscope. Purification of each sample was considered as finished when the wolframite concentration was higher than 95% (w/w). The location of deposits and approximate contents of main impurities of wolframites are indicated in Table 1.

Selection of samples was performed in order to include a wide range of the ratio of divalent metals present in wolframites (Fe/Mn + Fe). Iron is found in wolframite (structural Fe) and in several impurities (non structural Fe). The analytical method used in this work allowed to determine the total iron (structural and non structural), so wolframite iron was the difference between the value obtained by chemical analysis and the content belonging to impurities. Non structural iron estimation was made from the content of impurities determined in samples (Table 1). For manganese, it was not necessary to consider impurities since the wolframite was the only mineral species identified in all the samples that contained this metallic element.

Scheelite ($CaWO_4$) presence was established in all wolframite samples. Tungsten determined by chemical analysis included the metallic element contained in wolframite and

Table 1
Location and main impurities of natural wolframites used in this work

Sample	Location	Impurities (associations)
1	San Martín (San Luis)	Scheelite (<1.0%), quartz (1.5–2.5%), feldspars–micas (1.5–2.5%), pyrite (<1.0%)
2	Faltriquera (La Rioja)	Scheelite (1.5–2.5%), quartz (1.5–2.5%), pyrite (<1.0%), hematite (<1.0%)
3	Los Cóndores (San Luis)	Scheelite (1.5–2.5%), quartz (1.5–2.5%), pyrite (0.5–1.5%), limonite (<1.0%)
4	San Martín (Río Negro)	Scheelite (<1.0%), pyrite–chalcopyrite (1.5–2.5%), blende–arsenopyrite (0.5–1.5%), quartz (<1.0%)
5	Arrequintin (San Juan)	Scheelite (<1.0%), pyrite–chalcopyrite (0.5–2.0%), quartz (<1.0%), feldspars–micas (<1.0%), apatite (<1.0%)

Table 2
Chemical composition of wolframite samples as % w/w of Mn, Fe and WO_3

Sample	Mn	Fe	WO_3	Fe/Fe + Mn
1	1.1	16.5	72.4	0.94
2	2.1	15.6	73.3	0.88
3	7.9	9.7	72.7	0.55
4	13.3	4.3	73.1	0.24
5	14.7	2.9	72.8	0.16

Table 3
Cell dimensions in Å of wolframite samples and series end-members of the solid solution

Sample	*a*	*b*	*c*
Ferberite	4.734	5.708	4.965
1	4.746	5.719	4.963
2	4.751	5.723	4.965
3	4.785	5.732	4.975
4	4.813	5.745	4.986
5	4.828	5.762	5.004
Hübnerite	4.835	5.758	4.999

in scheelite. With the same methodology applied for iron, the tungsten corresponding to scheelite was deducted. Table 2 shows the chemical composition of the five studied wolframites. About 90% of each sample had a particle size between 125 and 210 μm.

Chlorinations were made with chlorine (chlorinating agent) and sulphur dioxide (reducing agent). The chlorination equipment used was composed of a vertical reactor with a static bed, a premixing chamber of gases at the reactor bottom and three cylinders (chlorine, sulphur dioxide and nitrogen) with its control valves and flowmeters. The excess of reactive gases and volatile reaction products were bubbled in $Ba(OH)_2$ solution at the reactor exit.

The reactor was heated by an electric furnace with temperature control. The test temperature was reached while a nitrogen flow circulated. When the system was stabilized to the selected temperature, nitrogen was replaced by reactive gases maintaining the same flow rate during the time corresponding to that test. Then, the furnace was turned off and cooled down to reach the room temperature while nitrogen circulated again. Reaction temperature was measured by a thermocouple and displayed on a digital thermometer.

Each test was made with 1 g of sample, so that the bed thickness did not present resistance to the gaseous flow. The sample was placed into the reactor on a ceramic fiber (kaowool). Such fiber, besides its function as support, made it possible the homogenization and heating of the gaseous flow (inert gas and reactive gases). By means of specific tests, it was established that a flow rate of 500 ml min^{-1} (inert gas or reactive gases) did not cause fluidization of the bed.

3. Results and discussion

3.1. Structural aspects of wolframite samples

Cell dimensions for studied wolframites are given in Table 3. Wolframite structure may be described as made up of hexagonal close packed oxygen atoms with some octahedral sites filled in an orderly way with tungsten(VI), iron(II) and manganese(II). A unit cell has half of the oxygen atoms coordinated to two tungsten atoms and half coordinated to two divalent cations. This atomic arrangement is adopted by divalent cations with ionic radii lower than 0.85 Å and it is maintained for the whole of wolframite specimens (Sleight, 1972). The different ionic radii of manganese(II) ($r = 0.83$ Å) and of iron(II) ($r = 0.78$ Å) produce a change of cell parameters depending on the ratio of divalent metals (Fe/Fe + Mn). Variations of cell dimensions were minimum, which allowed to assume that the bond length between each divalent metal and oxygen is very similar for all samples.

3.2. Chlorination process

Selection of chlorination experimental conditions (amounts of chlorine and sulphur dioxide, reaction time and temperature) was carried out in order to study the different behavior of wolframites. Reagent amounts that correspond to the reaction stoichiometry to form tungsten oxychloride and chlorides of divalent metals were determined from an average chemical composition of the five samples. Such amounts, for 1 g of sample, were: 0.45 g (142 ml NTP) of chlorine and 0.40 g (140 ml NTP) of sulphur dioxide. The chlorine adsorption on the reactive solid surface is low (Réti et al., 1987), and for this reason, it is convenient to add a large excess of chlorinating agent as an alternative to minimize the influence of such stage. With this purpose, 300 ml min^{-1} of chlorine were used. This flow is twice to that required to fulfill the reaction. Mixture of reactive gases was completed with the addition of 200 ml min^{-1} of sulphur dioxide to obtain a total flow rate of 500 ml min^{-1}. Such amount of reducing agent also forms a large excess of this reagent.

The effect of the reaction time and temperature on tungsten(VI) extraction was established through sample chlorination with higher iron(II) content (San Martín–San Luis) using flow rates above mentioned. Tungsten extraction was analyzed by means of two different ways, in one of them, the process was carried out as a function of reaction time at a unique temperature (value selected arbitrarily). In the other one, the temperature was the process variable but now, reaction time was maintained constant (value determined in the previous stage). Results obtained are shown in Figs. 1 and 2.

Tungsten extraction increased slightly after 5 min as it observed in Fig. 1, so that chlorinations during prolonged time were not performed. In a similar way, the temperature effect on tungsten extraction decreased at temperatures higher than 900 °C (Fig. 2). Such behavior was attributed to the wolframite exhaustion during the reaction. According to these results, the experimental conditions selected to make chlorinations were: 900 °C; 5 min; 300 ml min^{-1} of chlorine and 200 ml min^{-1} of sulphur dioxide.

Fig. 3 shows tungsten extraction in relation to the ratio of divalent metals contained in wolframite samples. The behavior determined reveals that tungsten extraction by chlorination increases with the iron(II) content. Wolframite cell dimensions and its tungsten contents (WO_3 = 72.4–73.3%) were similar, consequently, such mineralogical aspects are not significant to explain the system evolution. This induced to think that the mineral reactivity could be related only with chemical characteristics of divalent metals.

The formation of a non volatile reaction product or the presence of a liquid phase on the mineral surface affects its subsequent chemical attack (Bamford and Tipper, 1980). This is due to the fact that such product impedes the gas adsorption on the reactive solid surface. To evaluate this situation in the studied system, aggregation states of reaction products achieved from tungsten(VI), iron(II) and manganese(II) were determined at the reactor exit and in the ceramic fiber removed from the reactor.

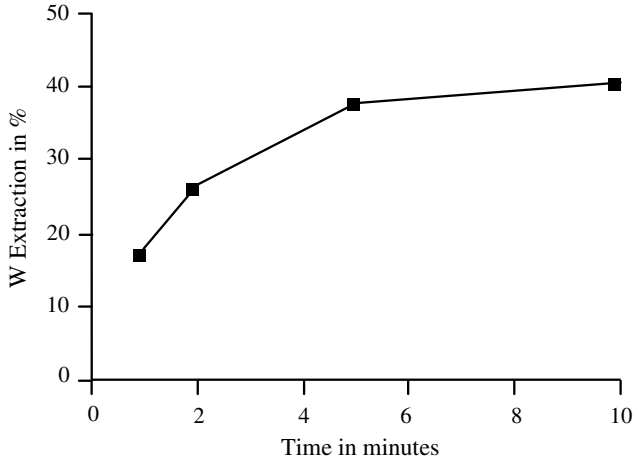

Fig. 1. Tungsten extraction from wolframite San Martín–San Luis in relation to the time at $T = 750$ °C and flow rates of 300 ml min^{-1} for chlorine and 200 ml min^{-1} for sulphur dioxide.

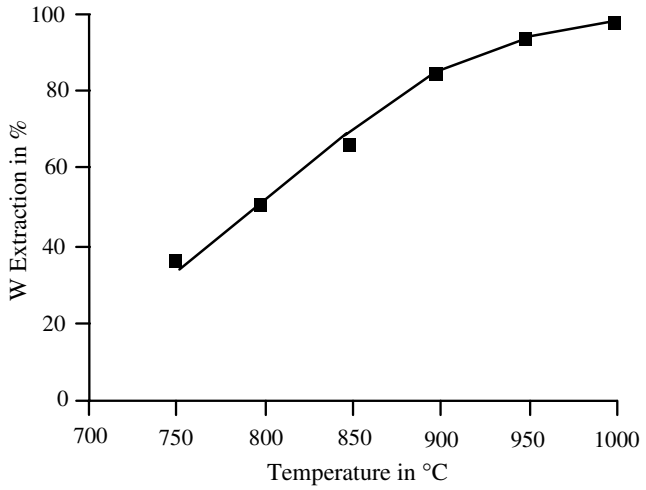

Fig. 2. Tungsten extraction from wolframite San Martín–San Luis in relation to the temperature at $t = 5$ min and flow rates of 300 ml min^{-1} for chlorine and 200 ml min^{-1} for sulphur dioxide.

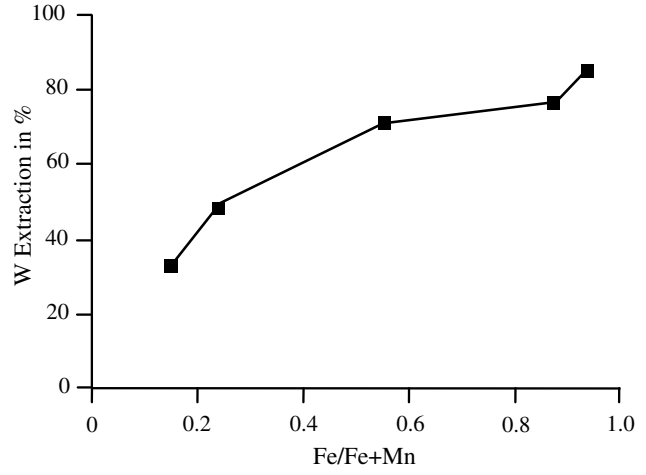

Fig. 3. Tungsten extraction as function of the ratio of divalent metals contained in wolframite samples at $T = 900$ °C, $t = 5$ min and flow rates of 300 ml min^{-1} for chlorine and 200 ml min^{-1} for sulphur dioxide.

At the reactor exit, very hygroscopic solid substances were collected. The chemical analysis of these substances allowed to establish that they were: WO_2Cl_2, $FeCl_2$ and $FeCl_3$. During chlorination, one of the products formed was $FeCl_2$ by reaction between iron(II) of wolframite and chlorine. Then, $FeCl_2$ was transformed to $FeCl_3$ due to the oxidizing action of chlorine (Nagata and Bolsaitis, 1987). As the gaseous flow shifts from the reaction zone (sample bed) its temperature decreases. When the flow temperature reaches 600 °C, the iron(III)-chloride predominant species is Fe_2Cl_6. This dimer has two iron atoms and two chlorine atoms in a planar ring (Fe_2Cl_2) and the other two pairs of chlorine atoms in a plane that is perpendicular to such ring (McArdle, 1981).

In the upper part of the reactor where hygroscopic solid substances were condensed, the temperature of the gaseous flow decreased to ~300 °C. $FeCl_3$ solidifies at 306 °C and at this temperature its partial thermal decomposition to $FeCl_2 + Cl_2$ can also occur. Such decomposition would explain the presence of both iron salts (McArdle, 1981).

The manganese(II) did not form any reaction product possible to be collected at the reactor exit as it occurred with tungsten(VI) and iron(II). From SEM observations, it was established that the grains of all residues had a uniform surface without superimposed particles (segregated) that suggests the presence of a non volatile reaction product. Fig. 4a shows residue grains obtained by chlorination of the manganese-rich wolframite (sample 5: hübnerite). To illustrate the surface behavior of other solid solution specimen, the SEM micrograph (Fig. 4b) corresponding to the chlorination residue of the iron-rich wolframite (sample 1: ferberite) was included. If we suppose that the formed reaction product with manganese was $MnCl_2$ (melting point = 650 °C and boiling point = 1190 °C), such salt would be in liquid state at 900 °C. In this way, the molten salt would be separated from the mineral that still remains without reacting and would flow by gravity through the ceramic fiber.

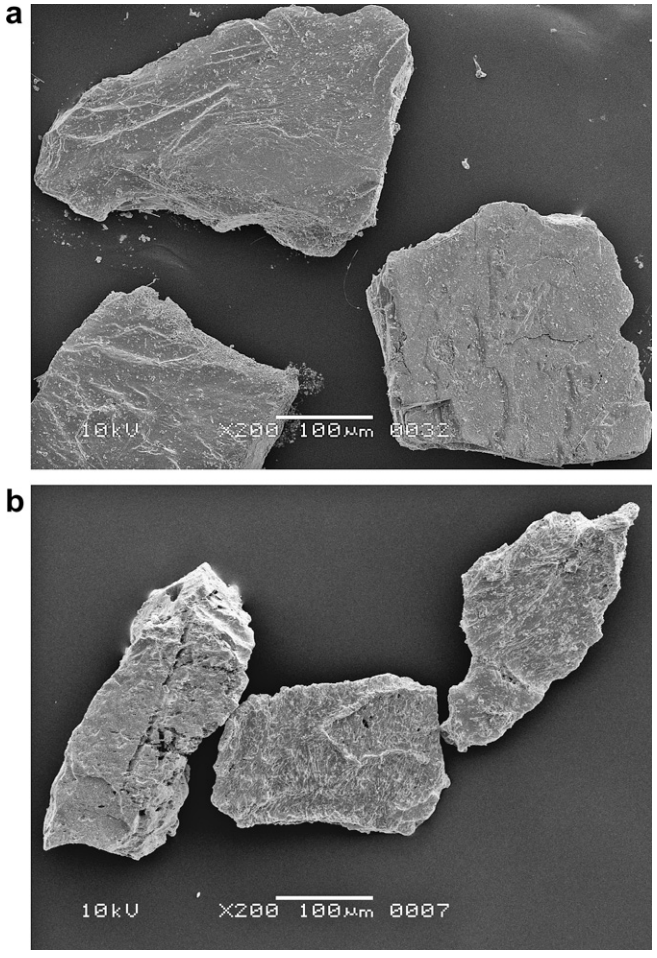

Fig. 4. Scanning electron micrographs of residues obtained by chlorination at 900 °C, 5 min, 300 ml min^{-1} for chlorine and 200 ml min^{-1} for sulphur dioxide: (a) wolframite Arrequintin–San Juan; (b) wolframite San Martín–San Luis.

SEM–EDX analysis of the ceramic fiber next to the zone in contact with the mineral revealed the presence of manganese and chlorine. This situation is concomitant with the fact that neither reaction product containing manganese at the reactor exit nor on the residue surface were identified. Manganese(II) oxidation would not be carried out by chlorine since the standard reduction potential of the metallic element is higher than the one of the chlorinating agent. This is an important difference with the iron(II) such as it was indicated, the chlorine causes the cation oxidation ($2FeCl_2 + Cl_2 \rightarrow 2FeCl_3$).

Standard reduction potentials (Eh) of both divalent metals and of chlorine are: 0.77 V for Fe(III)/Fe(II); 1.51 V for Mn(III)/Mn(II) and 1.36 V for $Cl_2(g)/2Cl^{-1}$ (Hunsberger, 1981). Aspects above mentioned (standard reduction potentials and boiling point) were used as evidences to establish that the reaction product effectively formed was $MnCl_2$ and it was not present on the residue at the moment of the SEM observation.

The released oxygen during chlorination reacts with sulphur dioxide to form sulphur trioxide. The presence of this volatile reaction product was determined through the $BaSO_4$ formation by bubbling of exit gases in $Ba(OH)_2$ solution ($Ba(OH)_2 + SO_3 \rightarrow BaSO_4 + H_2O$). Finally, it was established that the chlorination of the iron-rich wolframite and the manganese-rich wolframite leads to the formation of a same reaction product of tungsten (WO_2Cl_2). The global process can be interpreted according to

$$Mn_xFe_{1-x}WO_4(s) + 2Cl_2(g) + 2SO_2(g) \rightarrow WO_2Cl_2(g) + xMnCl_2(l) + (1-x)FeCl_2(g) + 2SO_3(g) \quad (1)$$

Although none of reaction products identified were observed on residues, the $MnCl_2$ behavior deserves a special attention. This is a substance that as it is in liquid state under our experimental conditions and by the reactor design (upward flow of gases), it remains more time in the reaction zone (sample bed) than volatile products. Thus, $MnCl_2$ would produce a double negative effect on the reaction rate. Firstly, chlorine adsorption on wolframite surface without reacting results partially obstructed by the liquid phase that flows around mineral grains. Secondly, the $MnCl_2$ presence makes it possible that equilibrium of Eq. (1) is reached with lower formation of the other three volatile products (Le Châtelier principle).

3.3. Thermodynamic considerations about iron oxychloride formation

Tungsten oxychloride, chlorides of both divalent metals and sulphur trioxide are obtained by wolframite chlorination. According to these reaction products, it is possible to state that the behavior of each specimen depends on

the facility of iron and manganese to react with chlorine. The free energy change (ΔG) for the formation of two chlorides permits to establish which divalent metal shows higher reactivity. These thermodynamic calculations are rigorously valid only for a closed system. If we assume that our reactor behaves as a dynamic system, ΔG values provide a reasonable evidence about the reactivity of each divalent metal.

ΔG determination was made in an analogous way as that one used by Gonzalez et al. (1998) to evaluate the chlorination of a columbite concentrate (a niobium and tantalum ore) that had 6.04% of Mn(II) and 7.20% of Fe(II). Such contents of divalent metals are similar to the ones of sample 3. In the mentioned work, chloride formation from each oxide was considered, obtaining a ΔG indicative value easier to be calculated ($Mn(Fe)O + Cl_2 \rightarrow Mn(Fe)Cl_2 + 0.5O_2$). Variations of free energy so determined using thermodynamic data published by Rosenqvist (1987) were: ca. $-50\ kJ\ mol^{-1}$ for the $MnCl_2$ and ca. $-25\ kJ\ mol^{-1}$ for the $FeCl_2$ at 900 °C. These values predict that conditions for occurrence of both reactions are not completely favorable and that $MnCl_2$ would be formed more easily than $FeCl_2$ at that temperature.

In wolframite, iron and manganese are coordinated to six oxygen atoms (octahedral symmetry) by metal–oxygen bonds. The $Fe(Mn)Cl_2$ formation involves rupture of cited bonds and transfer of electrons from oxygen to chlorine. ΔG calculation corresponding to M–O bond rupture in binary oxides should be made without taking into account any transfer of electrons ($Mn(Fe)O \rightarrow Mn(Fe)^{2+} + 0.5O^{2-}$). However, it is possible to determine an indicative value from the oxide decomposition in its elements ($Mn(Fe)O \rightarrow Mn(Fe) + 0.5O_2$). Obtained results show that the process is not spontaneous and rupture of the Fe–O bond ($\Delta G =$ ca. $+ 185\ kJ\ mol^{-1}$) would result more favorable if compared with the Mn–O bond ($\Delta G =$ ca. $+ 297\ kJ\ mol^{-1}$).

From a thermodynamic point of view, it was established that the combination of the metallic oxide with chloride is much more difficult for iron than for manganese. In order to explain the higher reactivity of iron-rich wolframites, it is analyzed if some reaction product of this element is easier to be formed than $FeCl_2$. Such formation facility is related with a reaction mechanism involving a lower formation of iron(II)–chloride bonds than to obtain $FeCl_2$. Analysis of possible reaction products revealed that the formation of iron(III) oxychloride (FeOCl) can occur with a partial rupture of M–O bonds, although to complete the reaction chlorine should oxidize to iron(II). As it was mentioned, iron(II) is the only one of the two divalent metals present in wolframite that may be oxidized by chlorine.

FeOCl was indicated as a reaction product formed during wüstite (FeO) chlorination with chlorine and with chlorine in carbon monoxide presence (Bertóti et al., 1987). More recently, wüstite chlorination with chlorine and carbon monoxide was made by Kamari et al. (1999). In the second paper, transformations of phases due to chlorination were illustrated by the equation: $4FeO(s) + 3Cl_2(g) + CO(g) \rightarrow 2FeCl_3(g) + Fe_2O_3(s) + CO_2(g)$. Authors mention the FeOCl presence but this substance was not included in the equation, not any mechanism of Fe_2O_3 formation was proposed.

It is known that FeOCl decomposes thermically in the range 230–430 °C according to: $3FeOCl(s) \rightarrow Fe_2O_3(s) + FeCl_3(g)$ (Dai et al., 2003; Szepvölgyi et al., 1988; Bertóti et al., 1987). For this reason, it is feasible to consider to Fe_2O_3 (hematite) present in a chlorination residue as an indirect evidence of FeOCl thermal decomposition. The occurrence of such decomposition would explain the FeOCl omission among reaction products corresponding to the last wüstite chlorination (Kamari et al., 1999).

According to two equations above mentioned (wüstite chlorination and thermal decomposition), the Fe_2O_3 amount obtained depends on the iron(II) initial content of the sample. In our system, the wolframite San Martín–San Luis (sample 1) has the highest iron content and would be the most appropriate specimen of the solid solution to determine the iron(III) oxide presence formed from FeOCl. The chemical attack of this wolframite was performed almost completely in the first minutes of chlorination (65% at 3 min and 86% at 5 min), so that the Fe_2O_3 formation would be produced at the reaction beginning. Notwithstanding, the residue analysis of the wolframite chlorination at 1–5 min did not show hematite (XRD) or the Fe/W ratio increase with respect to the original sample (EDX).

In order to verify the reactivity of the iron(III) oxide, chlorination (900 °C, $300\ ml\ min^{-1}$ of chlorine and $200\ ml\ min^{-1}$ of sulphur dioxide) of commercial Fe_2O_3 (Mallinckrodt, analytical reagent) was performed at 3 and 5 min. Iron(III) extractions were: 98% at 3 min and 99% at 5 min, values that indicate a reasonable agreement with those reported in other works (Kamari et al., 1999; Gennari and Pasquevich, 1996). The high reactivity shown by synthetic iron(III) oxide under experimental conditions used to make chlorinations allows to state that identification of superficial iron(III) oxide formed "in-situ" is not possible.

4. Conclusions

Chlorination of natural wolframites ($Mn_xFe_{1-x}WO_4$) with chlorine and sulphur dioxide was analyzed through the characterization of reaction products obtained in each case. Reaction products identified were: $WO_2Cl_2(g)$, $FeCl_2(g)$, $FeCl_3(g)$, $MnCl_2(l)$ and $SO_3(g)$. Likewise, it was established that almost all of them were continuously displaced by the upward flow of reactive gases. $MnCl_2$ was the exception, while this reaction product maintained the liquid state it moved downward.

Wolframite reactivity depends on the ratio of their divalent metals and results obtained show clearly a different behavior for each specimen of the solid solution. The maximum tungsten extraction was 86% for the sample with 94% Fe/Mn + Fe ($x = 0.06$) and the minimum tungsten

extraction was 36% for the sample with 16% Fe/Mn + Fe ($x = 0.84$). With a practical criterion, it can be said that the chlorination is very convenient to recover tungsten from iron-rich wolframites.

The variation of cell dimensions of wolframites with different content of divalent metals was minimum and this fact would not explain the unequal mineral reactivity.

$MnCl_2$ would be formed more easily than $FeCl_2$ according to the demonstration performed from thermodynamic considerations, which constitutes an opposite behavior to the one determined experimentally. The lower reactivity of manganese-rich wolframites was explained by kinetic arguments based on the liquid character of $MnCl_2$.

It was observed that iron(II) is the only one of the two divalent metals present in wolframite that is oxidized by chlorine and that the iron(III) oxychloride (FeOCl) formation can be performed with a partial rupture of the metal–oxygen bond. Even when main physicochemical characteristics of the system are favorable for the formation of such intermediate reaction product, not any evidence of its presence could be determined under experimental conditions used to perform chlorinations. This substance makes it possible to give an alternative explanation about the higher iron(II) reactivity with respect to manganese(II).

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