



Purification of talcs by chlorination and leaching

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ABSTRACT

The use of chlorine in talcs deferritation has been studied in four samples taken from the province of Mendoza, Argentina. The techniques used in this process were thermogravimetry (TG), X-ray fluorescence (XRF), X-ray diffraction (XRD) and CieLab colorimetry. Experimental results show that the pyrometallurgical process of chlorination is an efficient method for removing Fe₂O₃ from talc, by volatilizing it as FeCl₃. Previous leaching of the sample with HCl 10% (w/w) produced the elimination of carbonates, and a slight iron removal. Quantitative elimination of iron, both in untreated samples and leached ones, was made by chlorination with chlorine gas 1:1 in nitrogen, at temperatures over 800 °C. Experimental results show that deferritation can remarkably improve mineral coloration.

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1. Introduction

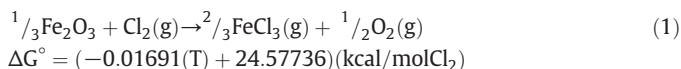
Talc is a hydrated magnesium silicate with the formula Mg₃Si₄O₁₀(OH)₂, which is widely used in industries due to its intrinsic properties, such as chemical inertia, softness, high thermal stability and low electrical conductivity. Argentinean talc market is being supplied almost entirely by talc from Mendoza and San Juan. Cosmetic and clay industries use importation talcs, which are purer than Argentine talcs due to their level of micronization and whiteness (Sarquis and González, 1998; Colombo, 2008).

The presence of iron, both in the surface of talc, and in the structure of clinocllore and accessory minerals, reduces talc refractory properties and diminishes its whiteness, which gives it an undesirable color, especially during calcination.

Studies on the reaction of Fe₂O₃ with Cl₂ have shown that the reaction can happen at approximately 650 °C, producing FeCl₃, which is volatile under these conditions. For this reason, it can easily be removed (Gennari and Pasquevich, 1996; Kanari et al., 1999a, 1999b; González and Ruiz, 2006; Kanari et al., 2010). The main aim of this work is to study the feasibility of using the pyrometallurgical process of chlorination as an alternative technique for removing iron from talc efficiently.

2. Thermodynamic analysis

A thermodynamic analysis of chlorination reaction of iron, present as an impurity, using HSC Chemistry for Windows 5.1 (HSC, 2003) was made. Thermodynamics calculations for the reaction of iron oxide and hydroxide phases from the mineral with chlorine show that chlorination is thermodynamically feasible at temperatures above 1000 °C. Eq. (1) corresponds to the free energy change per mole of chlorine for the chlorination of hematite, which is the main phase of iron remaining in the talcs after calcination in air and causing red coloration at high temperatures.



Studies on the reaction of ferric oxide with chlorine show that its occurrence starts at about 650 °C, this does not agree with its feasibility at 1000 °C. This difference lays on the fact that in flow systems, the FeCl₃ (g) and O₂ (g) generated by the chlorination are removed from the reaction zone, shifting the reaction to the right.

3. Experimental

3.1. Materials

The talc samples used in this work come from Mendoza, Argentina, and were provided by *Minera Cema S. A.* Four different samples were used, which were identified as T3, 72, C5 and 78.

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The global composition of the samples are shown in Table 1. The gases used in the different assays were chlorine 99.5% (Indupa, Argentina) and 99.99% nitrogen (AGA, Argentina).

3.2. Equipment

Experimental non-isothermal calcination assays were carried out, both in an inert atmosphere, and in a current of $\text{Cl}_2\text{-N}_2$, using a thermogravimetric system designed in our laboratory, which allows to perform thermogravimetric assays in corrosive atmospheres at temperatures of up to 1200 °C with masses of up to 5 g, with a sensitivity of 0.1 mg (Túnez et al., 2007). Isothermic calcination assays in currents of N_2 and $\text{Cl}_2\text{-N}_2$ were performed in a quartz tubular reactor. This reactor works under similar fluid dynamic conditions to the thermogravimetric system.

Measurements to determine talc samples chemical composition, variation of their composition after different assays, and above all, variation in iron content were carried out by X-ray fluorescence (XRF) with a Philips PW 1400 equipment. The X-ray diffraction (XRD) analysis was performed with a Rigaku D-Max-IIIIC equipment, Cu-K α , operated at 35 kV, 30 mA.

Colorimetric analyses in CieLab coordinates were performed with a HunterLab MiniScan EZ 4500 L equipment.

3.3. Procedure

Non-isothermic assays performed on the thermogravimetric system were carried out using masses of approximately 1 g of powder sample without previous treatment, a flow rate of N_2 of 50 ml/min for assays in inert atmosphere, and a flow rate of 50 ml/min of $\text{Cl}_2\text{-N}_2$ (50%) for chlorination assays.

The linear heating program was of 5 °C/min up to the final programmed temperature. Masses of 1 g with no previous treatment, a flow rate of N_2 of 100 ml/min and of 100 ml/min of $\text{Cl}_2\text{-N}_2$ (1:1) for assays in inert atmosphere and chlorination assays, respectively, were used for isothermic experiments in the quartz tubular reactor. A linear heating program of 10 °C/min was used until the final temperature was reached. The sample kept this temperature until the end of the time period specified for each assay. Once the reaction period was over, Cl_2 flow was interrupted, and the sample was purged with N_2 while the reactor cooled down.

4. Results and discussion

4.1. Characterization of talc samples

The results of the quantitative analysis of the four talc samples are shown in Table 1. The table shows that talc 78 has the highest content of Fe_2O_3 , thus the results of the purification assays performed by chlorination will be shown using this sample. It is interesting to note that similar results were obtained with the rest of the samples.

The characterization result of sample 78 by XRD (Fig. 1) evidenced the presence of talc "T", clinocllore "C", dolomite "D", and magnesite "M", since its lines of diffraction coincide with JCPDS cards 29-1493; 16-351; 36-426 and 8-479, respectively. The diffractograms of the other samples evidenced the presence of the same minerals, with variations in proportion. This is in agreement with the global composition; for

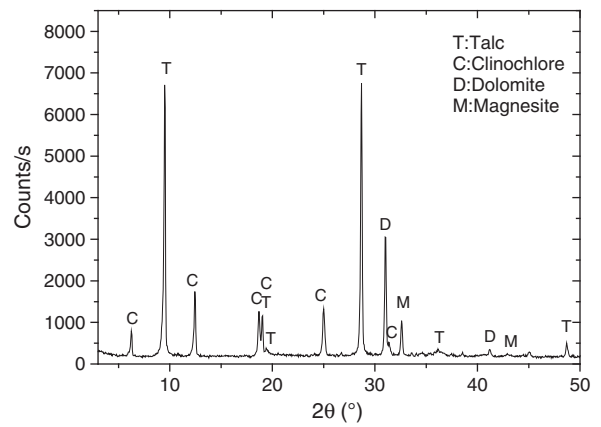


Fig. 1. Diffractogram of talc mineral 78.

example, sample 78 has the highest content of iron and aluminum, which coincides with a higher content of clinocllore found in this talc.

4.2. Non-Isothermal Thermogravimetry in N_2 and $\text{Cl}_2\text{-N}_2$

Non-isothermal calcination experimental assays of talc sample 78, both in currents of N_2 and $\text{Cl}_2\text{-N}_2$ mixture are shown in Fig. 2. The percentage loss of mass in talc with no previous treatment vs. temperature has been illustrated in this figure.

Analysis of Fig. 2 shows that the thermogram in N_2 can be divided into 3 regions of mass loss. The first region can be observed in a temperature range between 530 and 620 °C, and it is associated with a mass loss of 4.3% approximately. The second region can be noted in a temperature range between 650 and 780 °C, and it is the region corresponding to a mass loss of approximately 8.3%. The last region of mass loss can be observed in a range between 780 and 900 °C, and corresponds to a mass loss of approximately 2.6%.

The curve obtained during calcination in the flow of $\text{Cl}_2\text{-N}_2$ of talc 78 (Fig. 2) also shows three regions of mass loss. The first region can be observed in the range of 400 to 650 °C, after a slight mass increase and a mass loss close to 5.8%. The second region can be noted in a temperature range between 650 and 800 °C, and with a percentage of mass loss of approximately 7.6%. Finally, a continuous mass loss can be observed between 800 °C and 1000 °C.

With the purpose of finding out about the thermal transformations associated to different regions of mass loss observed in the thermograms, isothermic assays were carried out at different temperatures for 45 minutes, and residues were later analyzed by XRD. The results of these experiments show that the first mass loss observed in current

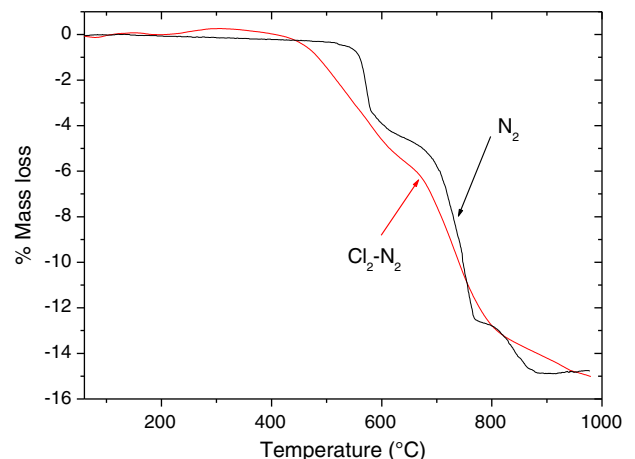


Fig. 2. Calcination in N_2 and $\text{Cl}_2\text{-N}_2$ of talc 78.

Table 1
Chemical composition (%w/w) of talc minerals use in the study.

Sample	CaO	MgO	SiO_2	Fe_2O_3	Al_2O_3	LOI
T3	3	30	43	3	3	18
72	3	30	48	3	3	12
C5	4	32	42	4	4	12
78	5	32	41	4.8	5	12

of N_2 (Fig. 2) belongs to total decomposition of the magnesite phase and to partial decomposition of clinocllore by interlayer dehydroxylation (Brindley and Chang, 1974). The second mass loss belongs to decomposition of the dolomite phase, and to the end of clinocllore phase decomposition. Finally, the last mass loss observed in current of N_2 belongs to decomposition of talc phase.

A similar isothermal treatment performed in current of Cl_2-N_2 showed a decrease of decomposition temperatures in different carbonate phases. This agrees with thermodynamic predictions since the formation of $CaCl_2$ and $MgCl_2$ is favored over that of CaO and MgO respectively. The first stage of the mass loss observed in current of Cl_2-N_2 (Fig. 2) belongs to partial clinocllore decomposition and total magnesite and dolomite decomposition. An increase of mass is produced during this process due to the formation of $CaCl_2$ and $MgCl_2$. The latter are products of magnesite and dolomite decomposition, which—depending on the reaction temperature—remain on the mineral, either in solid or liquid state (HSC, 2003). For this reason, the values of percentage mass loss in current of N_2 with respect to Cl_2-N_2 do not coincide. The second mass loss observed in current of Cl_2-N_2 belongs to total decomposition of clinocllore and talc, whose decomposition temperature diminishes due both chlorination of iron, present in the mineral as an impurity, and volatilization of ferric chloride that begin in this zone as well.

The third zone of mass loss that begins to stand out above 800 °C is due to quantitative mineral deferrification caused by the removal of the iron in the structure of clinocllore and partial volatilization of magnesium chloride, which is important at temperatures above 950 °C.

4.3. Analysis of iron in chlorination residues

Fig. 3 shows the results of the iron analysis performed by XRF on the talc 78 sample residues which result from the treatment with chlorine at different temperatures and reaction times. It can be noted that a considerable increase in Fe_2O_3 extraction is produced in the temperature range between 600 and 700 °C. This is due to the fact that the iron that is being removed in this temperature interval is the most reactive one, such as the iron, part of secondary minerals like pirite, which is finely dispersed in talc (Kanari et al., 1999a, 1999b).

Iron extraction shows little variation at 800 °C when compared to the one observed at 700 °C. These results can be attributed to the fact that the remaining Fe_2O_3 is difficult to remove, since it is strongly adsorbed in the surface of minerals with laminar structure. A similar behavior has been observed during deferrification of clays (González and Ruiz,

2006; Orosco et al., 2011), which need chlorination temperatures over 800 °C in order to reach proper whiteness.

Quantitative extraction of the iron present in talc 78 happens at temperatures over 900 °C, where clinocllore decomposition has occurred.

Fig. 3 also highlights that the highest level of iron extraction happens during the first 15 minutes of reaction, and that this does not depend on temperature. This phenomenon is produced because the products of the reaction act as a barrier for chlorine gas, particularly calcium chloride and magnesium chloride, which are generated by decomposition and chlorination of carbonates.

4.4. Effect of leaching agent

A series of talc 78 samples were exposed to the action of HCl 10% w/w for 24 h. The amount of acid used was greater than the amount necessary to achieve total decomposition of carbonates. Total decomposition of carbonates in the sample, and decomposition of sulphurs—like pirite—was made with this treatment. The analysis by XRD of the leached mineral only showed the presence of talc and clinocllore.

The leached sample was filtered and washed, first with acidulated water, and then with distilled water, several times. The filtered sample was dried at 60 °C, and subjected to thermogravimetric assays in currents of N_2 and Cl_2-N_2 . Fig. 4 shows the results of these assays. It can be observed that the calcined sample in a N_2 current has two zones of mass loss. The first one is produced in the same temperature range observed in the first stage of Fig. 2. The difference is that in the latter, mass loss is only due to partial dehydroxylation of clinocllore (Brindley and Chang, 1974). After this first stage, a light mass loss is produced up to approximately 800 °C; this temperature belongs to total decomposition of clinocllore. Finally, a mass loss corresponding to talc decomposition is observed at temperatures higher than 850 °C. In both cases, mass loss is exclusively due to clinocllore and talc decomposition, since magnesite and dolomite have been removed. Then, after comparing the data in Figs. 2 and 4 by masses balances, it was possible to determine that the mineral has the following approximate composition: talc, 47.5%; clinocllore, 9.1%; magnesite, 8.6%; dolomite, 15.2%; others, 19.6%. This ore composition corresponds to the values expressed as oxides in Table 1.

Fig. 4 also shows that, just like in Fig. 2, the effect of chlorine over the leached mineral produces a light decrease of temperature in clinocllore decomposition, and a mass loss lower than the one observed in current of N_2 . This is due to the mass gain produced by the formation of $MgCl_2$. It is also observed a decrease in the temperature of talc decomposition, and a higher mass loss at high temperatures due to quantitative volatilization of iron and $MgCl_2$.

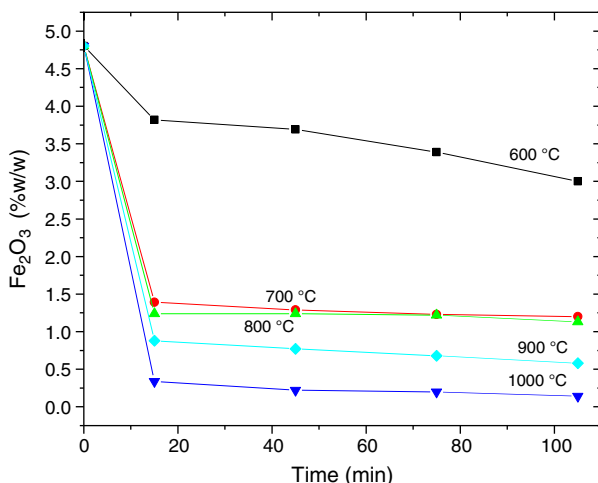


Fig. 3. Fe_2O_3 in residues of talc 78.

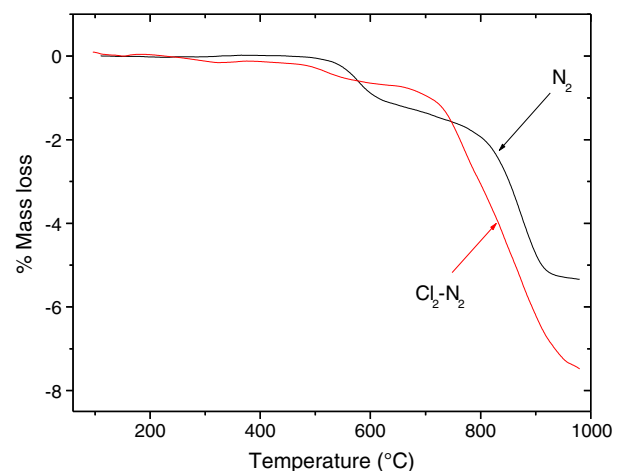


Fig. 4. Calcination in N_2 and Cl_2-N_2 of leached talc 78.

Table 2 shows the results of the XRF analysis of iron content in talc residues which were leached and later exposed to the action of chlorine and nitrogen, and to different temperatures for 120 minutes.

The results in Table 2 indicate that the sample of talc 78, which was leached and calcined in a stream of nitrogen, apparently has as much Fe_2O_3 as the untreated sample (Table 1). However, in Table 2, the amount of iron refers to the mass of mineral after the leaching process, during which 23.8% of mass was lost. Consequently, it is clear that a partial extraction of iron was also produced, especially from pyrite and other secondary minerals with iron content (Sarquís and González, 1998).

Data in Table 2 also show that, during the chlorination process of the leached mineral, a lower iron extraction is produced in relation to the extraction achieved under the same experimental conditions with untreated mineral, even when the difference in mass due to carbonates is considered. For example, the percentage of Fe_2O_3 w/w in the chlorination residue of leached talc is 2.09 at 900 °C, and after 120 minutes, whereas the percentage of Fe_2O_3 w/w in the chlorination residue of the untreated talc is 0.58. This result is probably due to the fact that the amount of CaCl_2 and MgCl_2 —produced from the reaction between carbonates and chlorine—is lower, and thus the additional chlorinating action that these chlorides have on the mineral is also lower. This phenomenon has been proved by experimental methods.

4.5. Colorimetric analysis of chlorinating residues

The redness that may occur in talcs after calcinations is indicative of iron content dispersed among particles, in the form of oxides, hydroxides, pyrite, etc. In order to quantify discoloration and clarity, spectrometric analysis of the color space $L^*a^*b^*$ (also known as CIELAB) were performed, where the parameter L^* indicates the dimension of clarity and coordinates a^* and b^* define the chromaticity plane whose center is neutral or gray. The higher the value of L^* , the lighter the color. Coordinate $+a^*$ indicates shift to red and $-a^*$ is shift to green; $+b^*$ indicates shift to yellow and $-b^*$ is shift to blue. This is known as opponent chromatic system, whose values vary between 0 and 100. The colorimetric analysis of talc samples calcined in N_2 and Cl_2 showed important variations in color and clarity parameters, as it is illustrated in Table 3. Calcinations in air, at the same temperature and at the same time, were also performed by using a conventional muffle furnace, since the coloration acquired by talc after thermal treatment in air determines quality.

Table 3 clearly shows that the mineral with no treatment and dried at 100 °C has little coloration and clarity over 80. The mineral, leached and dried at 100 °C, showed an improvement in the clarity parameter, and a light change of color to yellow.

Thermal treatment carried out at different temperatures and in currents of nitrogen and air produced similar results, with a clarity loss of 70—value slightly influenced by temperature—in relation to the original sample and the L^* value. The color parameters showed a tendency towards red, and a mostly towards yellow.

Thermal treatment of the leached mineral in current of N_2 slightly improves the clarity parameter in relation to the unleached mineral calcined under the same conditions.

Table 2
 Fe_2O_3 content in the residues leached and calcined talc 78.

Temperature (°C)	Gas	Fe_2O_3 (% w/w)
100	N_2	4.5
600	N_2	4.55
600	Cl_2/N_2	3.88
800	Cl_2/N_2	3.28
900	Cl_2/N_2	2.09
1000	Cl_2/N_2	1.19

Table 3
Colorimetric analysis of talc samples calcined in N_2 , air and Cl_2 .

Sample	Temperature (°C)	Gas	Time (min)	L^*	a^*	b^*
Talc 78	100	N_2	120	82.23	-1.46	0.96
Leached talc 78	100	N_2	120	87.79	-0.82	6.06
Talc 78	600	N_2	120	71.34	4.68	14.84
Talc 78	600	Air	120	68.24	4.14	13.72
Leached talc 78	600	N_2	120	73.2	3.22	13.33
Talc 78	600	Cl_2	120	58.88	9.81	17.21
Leached talc 78	600	Cl_2	120	77.37	3.18	11.27
Talc 78	800	N_2	120	69.83	5.67	16.37
Talc 78	800	Air	120	68.69	5.08	14.76
Leached talc 78	800	N_2	120	70.25	8.53	19.95
Talc 78	800	Cl_2	120	83.07	6.74	24.41
Leached talc 78	800	Cl_2	120	74.71	10.8	22
Talc 78	900	N_2	120	71.49	8.25	21.48
Leached talc 78	900	N_2	120	73.17	8.94	20.68
Talc 78	900	Cl_2	120	94.92	0.91	8.04
Leached talc 78	900	Cl_2	120	84.92	4.7	15.93
Talc 78	1000	N_2	120	70.7	6.69	19.65
Talc 78	1000	Air	120	71.19	9.04	22.76
Leached talc 78	1000	N_2	120	71.92	5.85	18.56
Talc 78	1000	Cl_2	120	93.29	-0.36	1.3
Leached talc 78	1000	Cl_2	120	89.45	1.41	9.86

Thermal treatment in current of Cl_2 produces notable differences if compared to calcination in N_2 , both in the mineral with no previous treatment, and the leached mineral. The presence of Cl_2 at 600 °C slightly affects the clarity parameter in minerals with no previous treatment. This might be due to the oxidating action of this gas and the presence of oxygen, which normally accompanies technical grade Cl_2 . In this way, oxidation of iron present in the sample is more easily produced.

Calcinations in air at 600 °C also produces a slight decrease of the clarity parameter in relation to calcination carried out in nitrogen. This is probably due to a higher level of iron oxidation in air.

Thermal treatment carried out in Cl_2 atmosphere, in a temperature range between 800 and 1000 °C, notably favors both decoloration and increase of clarity. This phenomenon is more notable as temperature rises. These results agree with the decrease of iron content in residues, which was observed in Fig. 3.

The results illustrated in Table 3 also indicate that previous leaching of the mineral does not help decoloration at temperatures over 800 °C, probably due to the lack of additional chlorinating reaction of CaCl_2 and MgCl_2 which are products of dolomite and magnesite decomposition.

5. Conclusions

The pyrometallurgical process of chlorination has proved to be an efficient method for removing Fe_2O_3 from talc. Extraction of the adsorbed iron, such as the iron present in secondary metals, can be obtained by volatilization in the form of FeCl_3 . Previous leaching of the sample produced total elimination of carbonates and partial leaching of iron, but it did not produce improvements in the elimination of strongly adsorbed iron, such as the one present in clinocllore structure.

The experimental results obtained permit to determine that the ideal conditions for achieving an important extraction of iron, without producing a magnesium loss, are a temperature of 900 °C and a reaction time of 15 min. The impurities contained in Argentinean talcs limits their use because of undesired red coloration in calcined products such as steatite ceramics and those that contain talc in its formulation. The implementation of the procedure described in this paper will allow a better use of these talcs by the removal of such impurities.

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