

# Bleaching of kaolins and clays by chlorination of iron and titanium

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## Abstract

The quality of the clays and over all kaolin is measured in function of iron content, since this element gives an undesirable reddish color to this type of minerals. The use of chlorination for iron and titanium removal from different clay and kaolin minerals, used in Argentinian ceramic industry, has been investigated to establish reaction mechanisms, precautions and optimal conditions to bleach the clays. The method consists of the calcinations of the pellets in a flow of chlorine gas at temperatures between 700 and 950 °C, to remove the iron and the titanium by volatilization of the respective chlorides. Isothermal and non-isothermal chlorination assays were made and the effects of the temperature, reaction time, and carbon content in the sample over the bleach of the minerals and the phase transformations suffered by these minerals during the chlorination step were investigated. The removed amounts of iron and titanium were determined by X-ray fluorescence, the phase transformations were followed by X-ray diffraction and the samples' bleaching was established making an analysis of the space of the color by the spectrophotometric method CIELAB. Also, a thermodynamic analysis of the system using HSC Chemistry for Windows software was made. The experimental results show that for red clay with high colloidal iron content, the optimum working temperature for the iron quantitative removal, without aluminium loss, is close to 850 °C, in controlled atmosphere free of O<sub>2</sub> and H<sub>2</sub>O; lower temperatures require long reaction times. The extraction of titanium is not quantitatively achieved, as that of iron, even for long reaction times, because this element is present in different structures, with the consequent variation of its reactivity. The content of carbon and organic matter in the clays, in the case of the San Luis red clay, is enough for extraction improvement. However, the optimum concentration of carbon can vary depending on the type of clay and the amount of Fe<sub>2</sub>O<sub>3</sub> in the mineral. The formation of phases such as α-Al<sub>2</sub>O<sub>3</sub>, a product of chlorination, increases the piece hardness. The methodology used in this work allows for obtaining a great improvement in the color of the final product of the firing, achieving ceramic materials with notable whiteness, even with red clays.

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## 1. Introduction

The term kaolin is used to refer to white clays whose principal mineral is kaolinite (Al<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub>). Its particles are usually hexagonal and 0.05 to 10 μm in

diameter (0.5 μm in average). Since this mineral is a product of the decomposition of feldspars and micas present in pegmatites micaceous schist, it is usually accompanied by other minerals such as quartz, sulfur, feldspars, micas and iron and titanium oxides, among others (Avgustinik, 1983; Norton, 1983). Kaolin deposits are classified as either primary or secondary. Primary kaolins result from residual weathering or hydrothermal alteration and secondary kaolins are

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sedimentary in origin. The three major areas of sedimentary kaolin production in the world are Georgia and South Carolina in the United States and the lower Amazon basin in Brazil; and of primary kaolin is the Cornwall area of Southeastern England (Murray, 2002).

The main uses of kaolin are: paper filling and coating 45%; refractories and ceramic 31%, fiberglass 6%; cement 6%, rubber and plastic 5%, paint 3%, others 4% (Murray, 2002).

Clays usually exhibit kaolinite as principal mineral, but with a lower granulometry and crystallinity than kaolin. Kaolinite can be accompanied by other clay minerals such as montmorillonite, illite and aluminum hydrated oxides such as boehmite, gibbsite, diasporite, and amorphous hydrated oxides among others. These minerals are formed from alteration of siliceous, glass-rich volcanic rock such as tuffs and ash deposits. Clays possess organic matter, generally lignite, as well as other colloidal minerals that confer characteristic colors. Red clays have ferric oxide, in minerals such as hematite, magnetite and amorphous hydrated oxides, among others (Norton, 1983; Avgustinik, 1983).

The beneficiation methods of kaolin minerals depend on the amount and nature of the mineral impurities associated to kaolin. Most of these minerals are extracted from open-pit mines by motor scrapers and then mixed with water and dispersants to form slurry. The coarse particles can be removed by centrifugation, decantation or filtration, depending on the particle size for processing. Coarse iron removal is performed by means of a magnetic separator, and a cake is then obtained by filter-presses which can be dried to remove remaining water. Clay minerals can be beneficiated or commercially used in the form of balls, as they are extracted. The processes for the beneficiation of clays can also include grinding, flotation and drying (Norton, 1983; Murray, 2002).

Iron is the main contaminant in clay and kaolin minerals. The removal of iron from kaolin is of particular importance in the paper industry, among others, where purity requirements are high. In these minerals, iron can form part or not of the kaolinite crystalline lattice. When it is inside, low concentrations do not affect coloration. On the other hand, in other secondary accompanying minerals in clays and kaolin such as hematite, goethite, maghemite and pyrite, iron can be removed by magnetic separation. The presence of colloidal iron, usually as hydrated oxides, affects more notoriously the white of clay and kaolin minerals when these are calcined, and its removal is more laborious.

The removal of colloidal iron from clays and kaolins is not an easy task, since it is strongly adsorbed to the mineral particles, and can also remain trapped in the

particles. The numerous iron extraction methods investigated can be classified into physical and chemical. The former makes use of separation techniques such as flocculation (Larroyd et al., 2002) and high-gradient magnetic separation (HGMS) (Maurya and Dixit, 1990; Raghavan et al., 1997; Chandrasekhar and Ramaswamy, 2002). The latter, on the other hand, use leaching agents alone or together with reducing agents (Veglio' and Toro, 1994; De Mesquita et al., 1996; Ambikadevi and Lalithambika, 2000; Atkinson and Fleming, 2001; Fabry and Kleindl, 2001). Their disadvantage is the high cost and the fact that they alter the plastic properties of clays, which are extremely important in clays used for ceramic making. Bioleaching methods are currently being investigated which make use of microorganisms (De Mesquita et al., 1996; Eun et al., 2002; Cameselle et al., 2003), which can act directly on the mineral, or through the carboxylic acids they generate.

The use of chlorination in extractive metallurgy procedures has notably increased in the past few decades and an increase in chlorine use in pyrometallurgical processes can be anticipated. This is due, among other reasons, to the elevated reactivity, low cost, variety and availability of chlorinating agents, as well as to the development of corrosion resistant materials and the simplicity of effluent treatment and recovery (Jena and Brocchi, 1997).

Chlorination of kaolin minerals has been investigated in order to remove impurities, mainly iron and titanium, to achieve a whitening of the mineral for later use in paper industry (Carpmael, 1928; Farbenindustrie Aktiengesellschaft, 1932; Jackson et al., 1966). Chlorination has also been investigated under different working conditions and in some cases, incorporating elements that favor the reaction in order to take advantage of this minerals as aluminum and silicon sources (Sebenik and Lippman, 1978; Wyndham and Terry, 1979; Roder et al., 1987; Jinki and Park, 1992).

The use of chlorination for the removal of iron and titanium from clay minerals, and particularly kaolin, has given excellent results. In these processes, high temperatures (700 to 1000 °C) are used, at which the dehydroxylation of kaolinite has already taken place giving as products metakaolinite, and, at higher temperatures, spinell and mullite-type phases. These transformations increase particle hydrophobicity, hardness and size by sintering. Minerals thus treated can be used in a number of industries, such as paper, PVC, rubber, plastic, adhesives, polishing and tooth paste, in which higher hydrophobicity makes these minerals more compatible with organic systems (Chandrasekhar and Ramaswamy, 2002).

The use of kaolin and clays in ceramics and refractories is the second most important industrial application of

these minerals (Murray, 2002). In these industries, the purity requirements depend on the type and quality of the manufactured product. In the industry of fine ceramics and refractories it is vital not to alter the natural properties of clay minerals, because the presence of organic matter and colloidal minerals give the pieces the necessary plasticity and resistance before the burning stage. Any previous chemical treatment will modify these properties, making magnetic separation the only recommendable treatment for these applications.

In this work we investigate the use of chlorination for iron and titanium removal of different clay and kaolin minerals used in the Argentine ceramic industry. The methodology is applicable to the molded pieces, in order to achieve whitening during burning without altering the properties of the minerals during piece molding. This methodology has been investigated and applied; however, the advances in the knowledge of chlorination permits to establish reaction mechanisms, precautions and optimal conditions to reach the desired objective.

## 2. Thermodynamic analysis

The thermodynamic analysis for chlorination with chlorine gas of silicon and aluminum from kaolinite and of titanium from rutile shows that chlorination is thermodynamically feasible at very high temperatures (above 1700 °C) because their oxides are highly refractory. The chlorination of colloidal iron, present in the form of hematite ( $\text{Fe}_2\text{O}_3$ ), magnetite ( $\text{Fe}_3\text{O}_4$ ), limonite ( $\text{FeOOH}$ ), or ferric hydroxide ( $\text{Fe}(\text{OH})_3$ ), is feasible at temperatures close to 900 °C. However, it has been experimentally found that in fixed bed and flow systems, hematite chlorination is achieved at temperatures close to 700 °C (Gennari and Pasquevich, 1996; HSC, 2003).

Fig. 1 shows a calculation of the equilibrium composition as a function of temperature and in excess of chlorine. Using the method of system energy minimization, calculations were performed from 1 mol of  $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$  (product of kaolinite dehydroxylation), 1 mol of  $\text{TiO}_2$  and 1 mol of  $\text{Fe}_2\text{O}_3$ . This composition differs from the experimental one, but is more useful for visualizing the theoretical prediction of the system. It was observed that:

- 1) The thermodynamically more stable species for silicon oxide correspond to quartz or to high temperature forms such as tridimite and cristobalite.
- 2) For aluminum oxide, the corundum species or  $\alpha\text{-Al}_2\text{O}_3$  corresponds to the most stable species. The Thermodynamic anticipates that these species are the most stable in the here studied temperature range.

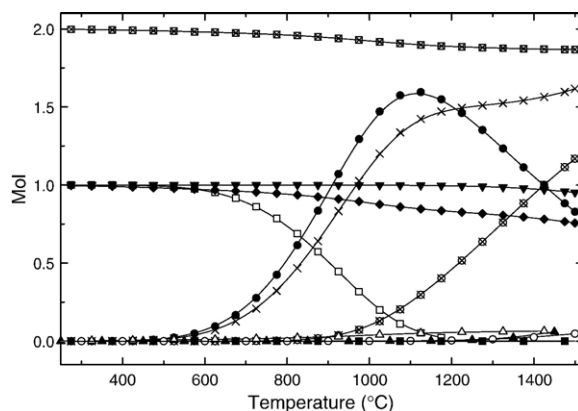


Fig. 1. Calculation of the composition of equilibrium as a function of temperature, in excess of chlorine, for the different species in the mineral. ■ :  $\text{SiO}_2$ ; ● :  $\text{FeCl}_3(\text{g})$ ; ▲ :  $\text{O}_2(\text{g})$ ; ▼ :  $\text{TiO}_2$ ; ◆ :  $\text{Al}_2\text{O}_3$ ; ○ :  $\text{FeCl}_2(\text{g})$ ; □ :  $\text{Fe}_2\text{O}_3$ ; △ :  $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ ; ⊗ :  $\text{TiCl}_4(\text{g})$ ; ⊠ :  $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ ; × :  $\text{AlCl}_3(\text{g})$ .

- 3) Species  $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$  (mullite) starts to form as a stable structure at higher temperatures.
- 4) The thermodynamic calculations show, for the  $\text{Fe}_2\text{O}_3$  species, that this oxide starts to be chlorinated above 600 °C, with total conversion at temperatures close to 1200 °C, for a system in equilibrium. Species  $\text{FeCl}_3(\text{g})$  is the thermodynamically most stable one between 600 and 1000 °C, while after 1000 °C,  $\text{FeCl}_2(\text{g})$  is the most thermodynamically favored.
- 5) Species  $\text{TiO}_2$  was observed to be highly resistant to chlorine, with chlorination starting in an appreciable manner above 1400 °C. A similar observation was made for  $\text{Al}_2\text{O}_3$ .
- 6) In the case of  $\text{SiO}_2$ , no  $\text{SiCl}_4(\text{g})$  formation was predicted.
- 7)  $\text{Cl}_2$  and  $\text{O}_2$  have not been included in Fig. 1 in order to keep the scale, since it was mentioned before, that  $\text{Cl}_2$  was considered in excess and  $\text{O}_2$ , in equilibrium with the system, is the product of the chlorination of the respective oxides.

It must be pointed out that the results shown in Fig. 1 correspond to a closed system. When working with flow systems, as the one here investigated, the formation of gaseous species is favored since they are partially removed from the reaction zone, thus shifting the equilibrium to the gas products.

The presence of organic matter in clay minerals is an important factor in chlorination with chlorine gas, because carbon takes part in the chlorination reactions combining with the oxygen of the oxide and thus thermodynamically favoring the reaction. Also, carbon has kinetic effects on carbochlorination reactions. Both the

thermodynamic and kinetic roles of carbon have been widely studied in a number of carbochlorination reactions, the latter effect being of marked importance (Gennari and Pasquevich, 1996; González, 1999; Vracar et al., 2000; González et al., 2002).

The thermodynamic analysis also shows that the presence of H<sub>2</sub>O in the gaseous phase is harmful for the chlorination of the metallic components, because of obtaining HCl(g), whose chlorinating action is lower due to its higher stability (HSC, 2003). The presence of water in these systems can come from the dehydration of clay or from the combustion of gases when working with furnaces heated with methane gas or other fossil fuel.

### 3. Experimental

#### 3.1. Materials

The materials used in this work were different clays and kaolins, the origin and characteristics of which are described in Table 1.

For the study of the effect of carbon, was used carbon black provided by Cabot Corporation. The gases used in the different assays were chlorine 99.5% (Indupa, Argentina) and 99.99% nitrogen (AGA, Argentina).

#### 3.2. Equipment

Fig. 2 shows a schematic representation of the equipment used for the chlorination experiments with a quartz tubular reactor.

For calcination in air, a conventional furnace was used. Unchlorinated and chlorinated samples, as well as those heated in

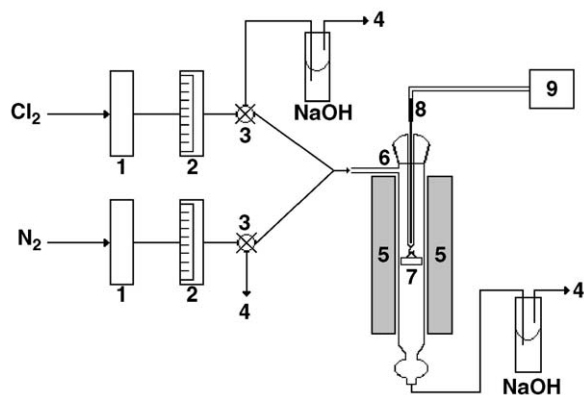


Fig. 2. Diagram of the experimental equipment. 1: H<sub>2</sub>SO<sub>4</sub> dryers, 2: flow-meters, 3: three-way valve, 4: venting, 5: electric furnace, 6: quartz reactor, 7: sample holder, 8: thermocouple, 9: thermometer.

air, were analyzed by X-ray diffraction (XRD), with a Rigaku D-Max IIIC equipment, Cu-K $\alpha$ , operated at 40 kV, 30 mA; and by X-ray fluorescence (XRF), with a Philips PW 1400 equipment. For color analysis in CIELAB (L\*a\*b\*) coordinates a Minolta CM-3600d spectrophotometer with integrator sphere was used, operated with standard D65 source, standard 10° observer and certified MgO reference blank.

#### 3.3. Procedure

The minerals under study were sieved at –100 mesh, in order to concentrate the clay minerals and subsequently were pelletized at 300 kg/cm<sup>2</sup> pressure. The pellets, which simulate the formed ceramic pieces, were then subjected to calcination assays. For each clay sample several pellets were prepared for

Table 1  
Materials used

Clay/Kaolin	Origin	Type	Main minerals detected by XRD	Uses
San Luis Red Clay	Potrero de los Funes, San Luis, Argentina	Red, plastic	Montmorillonite, kaolinite, illite, muscovite, quartz, feldspar group minerals, calcite	Ceramics
CADAM Kaolin	Amazonia, Brazil	White	Kaolinite	Paper
Burras Clay	Albardón, San Juan, Argentina	Red, semiplastic	Montmorillonite, illite, kaolinite, quartz, feldspar group minerals, calcite	Ceramics
Tapias Clay	Ullúm, San Juan, Argentina	Red, semiplastic	Montmorillonite, illite, kaolinite, quartz, feldspar group minerals, calcite	Ceramics
25 de Mayo Clay	Río Colorado, La Pampa, Argentina	Red, plastic	Montmorillonite, illite, kaolinite, quartz, feldspar group minerals, calcite.	Ceramics
Millenium Clay	Magallanes, Santa Cruz, Argentina	Light grey, semiplastic	Kaolinite, quartz, feldspar group minerals	Ceramics
Marquesita Clay	Trelew, Chubut, Argentina	Light grey, semiplastic	Kaolinite, quartz	Ceramics
Fortuna Kaolin	Río Negro, Argentina	Light grey	Kaolinite, quartz, calcite, feldspar group minerals	Ceramics
Gay Kaolin	Trelew, Chubut, Argentina	Light grey	Kaolinite, quartz, feldspar group minerals	Ceramics
Creta Clay	Trelew, Chubut, Argentina	Grey, semiplastic	Kaolinite, quartz	Ceramics

Table 2  
XRF analysis of air-calcined and chlorinated samples

Clay/Kaolin	% Fe <sub>2</sub> O <sub>3</sub>			% TiO <sub>2</sub>		
	Calcined in air	Chlorinated	Extraction (%)	Calcined in air	Chlorinated	Extraction (%)
San Luis Red Clay	1.84	0.025	98.5	3.43	1.10	67.9
Cadam Kaolin	1.39	0.122	91.2	1.95	1.67	14.3
Burras Clay	2.98	0.010	99.7	1.46	0.89	39.0
Tapias Clay	2.68	0.015	99.4	1.55	0.86	44.5
25 de Mayo Clay	3.97	0.010	99.7	1.43	1.22	14.7
Millenium Clay	0.59	0.002	99.7	1.99	1.56	21.6
Marquesita Clay	0.70	0.006	99.1	1.80	1.27	29.4
Fortuna Kaolin	0.38	0.026	93.1	1.52	1.19	21.7
Gay Kaolin	0.55	0.045	91.8	1.96	1.30	33.7
Creta Clay	0.78	0.011	98.6	3.33	1.53	54.1

the different assays. One pellet of each mineral was calcined in furnace to 950 °C with 5°/min heating rate, and then maintained at this temperature for 2 h. Using this procedure, a bisque was obtained in the temperature range at which coloration in white clays and kaolin is more appreciable.

Other pelletizing samples were introduced into the reactor shown in Fig. 2 (one per experiment), where they were calcined and chlorinated by two procedures, non-isothermal and isothermal, described below.

### 3.3.1. Procedure for non-isothermal chlorination

The pelletizing clay sample was calcined in N<sub>2</sub> flow by a 5 °C/min heating program up to 750 °C. Once this temperature was reached, Cl<sub>2</sub> gas was introduced at 20 ml/min, maintaining the sample at 750 °C and under Cl<sub>2</sub> flow for 2 h. After this period, heating was continued up to 950 °C, keeping this temperature for a further 2 h, in the same Cl<sub>2</sub> gas atmosphere. When heating was finished, the sample was purged with N<sub>2</sub> gas and the sample was allowed to cool inside.

### 3.3.2. Procedure for isothermal chlorination

The pelletizing clay sample was calcined in N<sub>2</sub> flow by a 5 °C/min heating program until the desired temperature was reached. Once the temperature was stabilized, Cl<sub>2</sub> was introduced at a given partial pressure, for a period preset for the experiment, and with a total gas flow of 20 ml/min. Once the

experiment was finished, the sample was purged with N<sub>2</sub> gas and the sample was allowed to cool inside.

For studying the effect of carbon, pellets of San Luis Red clay from San Luis were prepared, previously calcined in air at 800 °C and then mixed with 5% of carbon black in a rotatory mixer.

## 4. Results and discussion

XRF analysis of the different clay and kaolin samples used in this study showed that the percentage of Fe<sub>2</sub>O<sub>3</sub> varies between 0.5 and 4%, while that of TiO<sub>2</sub> is in the 1–3.5% range. It was observed that the total amount of iron and titanium in the mineral is not related with coloration either before or after firing. Iron can be present inside the clay crystalline structure, or in the form of free oxides; in the latter case, its presence is very important in the material coloration after firing.

### 4.1. Non-isothermal chlorination

XRF analysis of the Fe<sub>2</sub>O<sub>3</sub> content in the different pellet, air-calcined and non-isothermally chlorinated

Table 3  
CIELAB spectrophotometric analysis

Clay/Kaolin	L*		a*		b*	
	Calcined in air	Chlorinated	Calcined in air	Chlorinated	Calcined in air	Chlorinated
San Luis Red Clay	53.06	91.69	21.10	2.41	23.47	5.07
Cadam Kaolin	92.37	96.75	0.17	-0.14	8.36	3.39
Burras Clay	55.81	88.72	17.52	3.11	25.45	5.99
Tapias Clay	51.26	85.80	18.98	4.60	23.45	8.68
25 de Mayo Clay	55.17	88.93	22.39	4.71	26.87	9.73
Millenium Clay	87.61	93.52	3.78	1.27	9.09	3.20
Marquesita Clay	82.82	92.14	7.13	1.64	11.55	4.83
Fortuna Kaolin	87.87	94.46	3.63	1.18	8.02	3.00
Gay Kaolin	84.30	93.58	6.75	1.59	9.43	3.62
Creta Clay	79.57	89.23	5.14	0.81	15.15	2.02



samples indicated a marked decrease of  $\text{Fe}_2\text{O}_3$  in the chlorinated samples, achieving extraction percentages markedly above those obtained by other deferrification methods. The concentration of  $\text{TiO}_2$  also decreased in chlorinated samples, though in a lower proportion than  $\text{Fe}_2\text{O}_3$ . This is due to the fact that the titanium oxides are more refractory than iron ones, and thus their chlorination is less favored. The partial extraction of titanium observed in all the samples, even for long reaction times, indicates that this element is present in different structures, with the consequent variation of its reactivity. The quantitative extraction of titanium will certainly be achieved under more energetic conditions, which is beyond the scope of this work, because such conditions would lead the aluminum present in the clay to be also chlorinated. Indeed, this methodology has been investigated with the purpose of using clay minerals as alternative aluminum sources by means of carbochlorination. The concentration of  $\text{Al}_2\text{O}_3$  exhibited little change in chlorinated samples compared to air-calcined ones, observing in some samples a slight increment of the  $\text{Al}_2\text{O}_3$  concentration, probably due to the fact that it concentrates in the sample by effect of the volatilization of other components.

Table 2 shows the results of XRF analysis of the surface of the pellets calcined in air and chlorinated by the non-isothermal process. The decrease of the  $\text{Fe}_2\text{O}_3$  percentage is high in all the clay samples, and slightly lower in the kaolin ones. The white-baking in air in spite of the high iron content in Amazonian kaolin indicated that the iron present in this mineral forms part of the kaolinite structure. In all the samples, iron extraction from the kaolins was lower compared to clays. This can be attributed to the greater presence of iron inside the kaolinite net, which hinders chlorine access because it exhibits greater crystallinity and granulometry than clays. On the other hand, in the San Luis Red clay samples, iron forms hydrated oxides of easy access for chlorine. Removing the iron by this technique brings about discoloration and increase of the material clarity, achieving for all samples products of notable whiteness at the end of chlorination. Furthermore, the refractoriness is increased by eliminating most of the iron of the kaolinite crystalline structure.

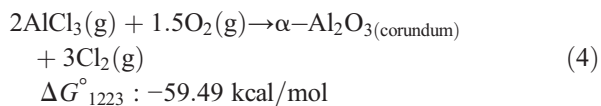
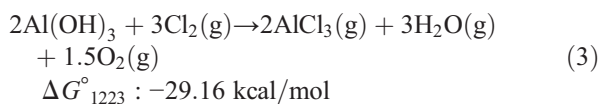
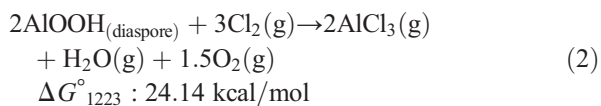
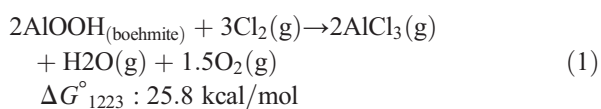
In order to quantify discoloration and clarity, spectrophotometric analysis of the color space  $L^*a^*b^*$  (also known as CIELAB) were performed, where the parameter  $L^*$  indicates the dimension of clarity and coordinates  $a^*$  and  $b^*$  define the chromaticity plane whose center is neutral 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. The results of this analysis are show in Table 3, in

which it can be observed that all chlorinated samples suffered notable discoloration and clarity increase.

XRD analysis of the Cadam kaolin samples is show in Fig. 3, which corresponds to an untreated (A), heated in air (B) and chlorinated by non-isothermal procedure (C) kaolin sample. In the untreated sample, only the kaolinite phase was clearly observed, the quartz and feldspar samples not being significant. In the air calcined sample, the anatase phase was clear, while the corundum phase was clearly seen in the chlorinated sample (JCPDS, cards numbers: 29-1488, 1995a; 33-1161, 1995b; 21-1272, 1995c; 42-1468, 1995d).

Diffractiongrams of montmorillonitic and illitic clays calcined in chlorine, exhibited the appearance of the cordierite ( $\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}$ ) and calcium silicoaluminate phases among others (JCPDS, card number 12-303, 1995e).

The effect of chlorine on the transformations of solid phases has been reported in other systems (González et al., 1998a,b,c; González et al., 2001a). The process by which these transformations occur is oxide recrystallization from the gaseous phase. High temperature chlorination of an oxide or mixture of oxides lead to obtaining the respective chlorides and oxygen in the first stage of the reaction. The formed chlorides and oxygen can be removed from the reaction zone in a flow system, or recombine to form oxides and chlorine gas again in a second stage. The second reaction stage will be favored as long as the reaction product is thermodynamically more stable. The reactions that are likely to occur from those aluminum minerals that normally accompany clays and kaolins are:



The  $\alpha\text{-Al}_2\text{O}_3$  phase (corundum) is thermodynamically stable and its formation in chlorine atmosphere from other phases has been experimentally found at temperatures close to the ones here used (Lopazo and Pasquevich,

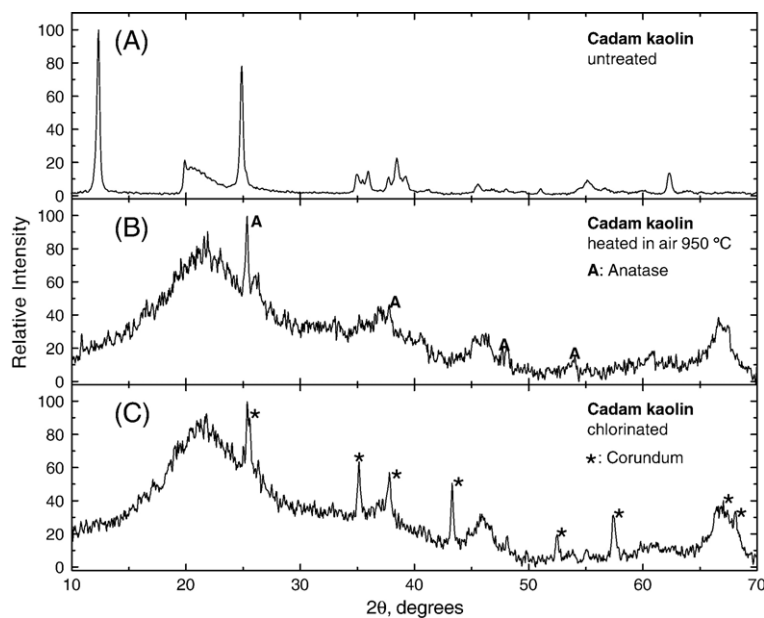


Fig. 3. XRD of untreated Cadam kaolin sample (A), calcined in air (B), calcined in chlorine current (C).

1997). From the thermodynamic calculations of Eqs. (1) (2) (3) and (4), it can be observed that chlorination of bohemite, diaspore or amorphous  $\text{Al}(\text{OH})_3$  and subsequent re-crystallization of  $\alpha\text{-Al}_2\text{O}_3$  is a thermodynamically favored process at 950 °C, with global  $\Delta G^\circ$  of  $-33.69$ ;  $-35.35$  and  $-88.65$  kcal/mol of  $\alpha\text{-Al}_2\text{O}_3$  respectively. In chlorination processes, it is generally observed that for refractory oxides, the presence of chlorine favors the transformations of phases to stable forms of these oxides, when starting from other phases or species. These phenomena occur at lower temperature than the one observed in air calcination, and this is due to the fact that in the process of oxide re-crystallization there is a reaction in gaseous phase between the chlorides and the oxygen produced by the initial chlorination reaction. In the re-crystallization of oxides (reaction 4), the obtained solid will be the most thermodynamically stable one. For the particular case of alumina, corundum is the most stable phase. The corundum phase is not achieved through a transformation in solid phase in the temperature range studied, which demonstrates that this phase was obtained from re-crystallization from the gaseous phase. Even though the formation of  $\alpha\text{-Al}_2\text{O}_3$  together with  $\text{SiO}_2$  (quartz) is a thermodynamically feasible reaction from metakaolinite using chlorine gas as intermediate, its occurrence has not been demonstrated in these system, since no quartz or other silica forms were detected together with  $\alpha\text{-Al}_2\text{O}_3$ . This is currently being further investigated.

The appearance of the cordierite and calcium silicoaluminate phases may have taken place from the

$\text{CaCl}_2$  and  $\text{MgCl}_2$  species, which are in liquid phase in the studied temperature range, and therefore the formation mechanism may occur through a solid liquid reaction to give volatile and stable mixed oxidized compounds, as has been reported for other systems (González et al., 1998d; González, 1999). The appearance, in chlorine atmosphere, of the corundum phase in kaolinite and of cordierite in montmorillonitic and illitic clays has not been studied in depth yet.

#### 4.2. Isothermal chlorination

The study of chlorination at 750 °C on the pellets of San Luis red clay was performed in order to determine variations in color and iron and titanium content with time for a fixed temperature. It was found that after 15 min and chlorine partial pressure of 0.5 atm, the pellets look somewhat discolored. Greater chlorination times did not lead to variations in the surface color, but rather an increase of the discolored area thickness. This phenomenon can be observed in Fig. 4, which shows a cross section of the pellets subjected to isothermal chlorination at 750 °C, after different reaction times.

This figure clearly shows the superficial discoloration of the pellet, whose thickness increases with reaction time until total discoloration after 120 min of reaction time. These results were corroborated by XRF analysis of  $\text{Fe}_2\text{O}_3$  and  $\text{TiO}_2$  on the pellet surface after isothermal chlorination and, subsequently, by grinding the same pellet and analyzing it globally. In the first case, a

predominantly superficial analysis is obtained (up to the thickness values that X-rays can penetrate), while a global analysis is obtained from the ground homogenized sample. The results of the  $\text{Fe}_2\text{O}_3$  analysis are shown in Fig. 5. The figure shows that after 15 min of chlorination, the concentration of superficial iron is such that the pellet appears discolored and clarified. At long chlorination times, the superficial analysis approximates the global analysis, since the sample has been exposed to the  $\text{Cl}_2$  action long enough for the iron inside the pellet to be removed, which agrees with observations from Fig. 4.

The analysis of  $\text{TiO}_2$  in isothermal assays showed a rapid decrease of its surface concentration, from 3.43% to 1.47% (w/w), after 15 min. It must be pointed out that at longer times extraction was not markedly improved. For instance, for the same experimental conditions and superficial analysis, a final concentration of 1.23% was obtained after 60 min. This result can be attributed to the fact that titanium is found in different crystalline structure with different reactivities to chlorine. The anatase phase was not detected by XRD in the chlorinated samples, which indicates that this phase is attacked during chlorination.

The concentration of  $\text{Al}_2\text{O}_3$  did not change appreciably, with a slight increase mainly due to iron volatilization, similarly to what was observed in non-isothermal experiments. This result indicates that aluminum extraction from these minerals by this methodology requires more energetic working conditions.

#### 4.3. Effect of temperature and carbon

A temperature increase always increases the chlorination reaction rate, when  $\text{Cl}_2$  is used as chlorinating agent.

When carbon combines with the oxygen of the metallic oxide to form  $\text{CO}/\text{CO}_2$ , it shifts the reaction to the formation of metallic chlorides. However, the kinetic effect of carbon in the chlorination reaction can sometimes be more important than the thermodynamic effect. This effect, as shown in other studies, is due to the generation

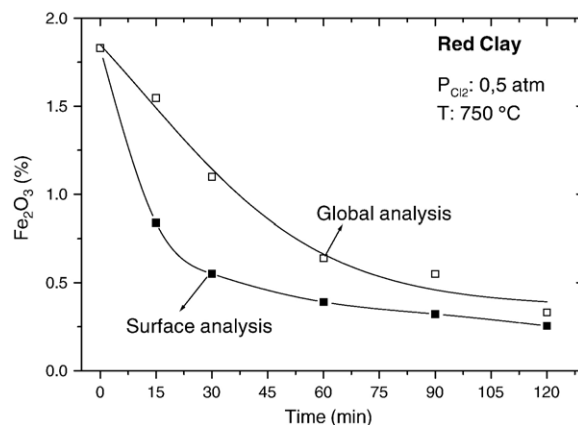


Fig. 5. XRF analysis of  $\text{Fe}_2\text{O}_3$  in the samples of isothermal assays.

of active chlorine species that intervene by favoring the chlorination reaction. Therefore, depending on the type, concentration and characteristics of the carbon, its catalytic effect on chlorination can be more important than its combination with  $\text{O}_2(\text{g})$ , although both reactions are normally present. This explains why at low carbon concentrations, as in clays, there can be free  $\text{O}_2$  in the reaction zone, capable or re-crystallizing new crystalline species such as  $\alpha\text{-Al}_2\text{O}_3$ .

The study of the effect of temperature and carbon was performed by a series of isothermal chlorination experiments on San Luis red clay pellets. After chlorination an analysis of the percentage of superficial  $\text{Fe}_2\text{O}_3$  on the pellets was carried out (Fig. 6). Three temperatures were investigated: 750, 850 and 950 °C. Curve (A) corresponds to chlorination of the clay with no previous treatment, in which the pellet is calcined in  $\text{N}_2$  until the desired temperature is reached, and then chlorinated for 15 min in a  $\text{Cl}_2\text{-N}_2$  mixture, with  $\text{Cl}_2$  partial pressure of 0.5 atm. Curve (B) corresponds to chlorination of the same clay calcined in air until the desired temperature is reached and then chlorinated as in (A). Curve (C) corresponds to a mixture of red clay with 5% of carbon black, subjected to

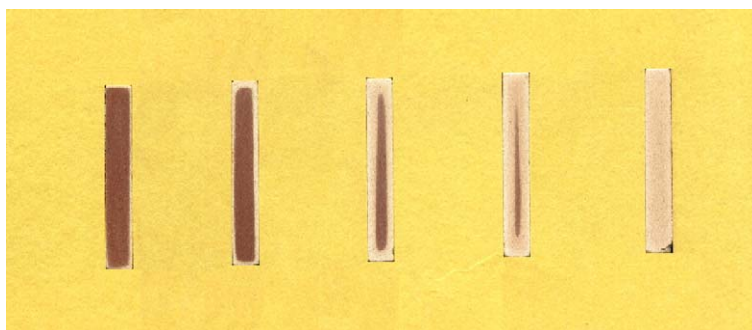


Fig. 4. Cross section of the pellets subjected to isothermal chlorination at 750 °C. From left to right: 15 min; 30 min; 60 min; 90 min; 120 min.



the same calcination and chlorination procedure as (A). Point (D) corresponds to an experiment at 850 °C, with the same calcination procedure as (B), but with chlorination performed in a  $\text{Cl}_2$ –air mixture with  $\text{Cl}_2$  partial pressure of 0.5 atm.

The results observed in Fig. 6 can be interpreted as follows. The optimum temperature for iron removal from the pellet is 850 °C; at lower temperatures there are thermodynamic and kinetic restrictions while at higher temperatures the sintering processes that decrease the reactivity of  $\text{Fe}_2\text{O}_3$  in presence of chlorine start. Lower temperatures require long reaction times, because the chlorination of  $\text{Fe}_2\text{O}_3$  with chlorine gas is more thermodynamically favored as the reaction temperature increases. It is recommended not to work at temperatures above 950 °C, because iron extraction by a solid gas reaction requires the diffusion of the chlorine gas to the metal. In order to avoid interferences with this process, the crystalline structure needs to be porous enough to allow chlorine access, and even of the iron that might be present in the clay crystalline structure. At temperatures above 950 °C a series of crystalline transformation starts such as the appearance of the spinell and mullite phases, sinterized and vitreous phases that will likely hinder the access of chlorine gas to the reaction points.

The difference between curves (A) and (B) can be due to the presence or not of carbon in the sample. A low carbon concentration, which is normal in clays, thermodynamically favors chlorination. This occurs when the sample is calcined in  $\text{N}_2$  and then chlorinated in a  $\text{Cl}_2$ – $\text{N}_2$  mixture (Curve (A)). In this case, most of the carbon remains in the clay and besides, any other type of non-volatile organic matter will carbonize and remain in the

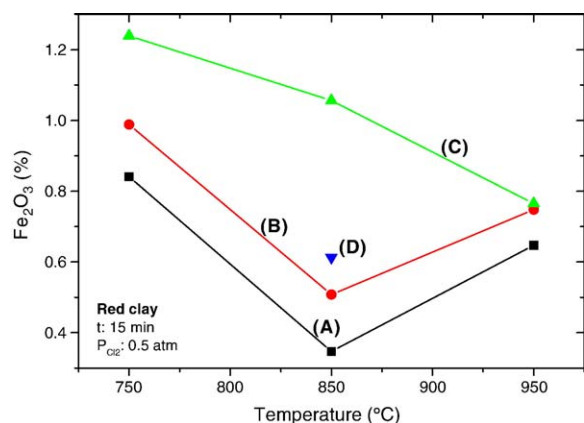


Fig. 6. Effect of the temperature, carbon and oxygen on the extraction  $\text{Fe}_2\text{O}_3$ . (A): Chlorination of previously untreated San Luis Red clay. (B): Chlorination of red clay, previously calcined in air. (C): Chlorination of red clay mixed with 5% of carbon (carbon black). (D): Chlorination of red clay in  $\text{Cl}_2$ –air mixture, with previous calcination in air.

sample. In curve (B), the carbon is consumed during calcination in air and therefore iron extraction was lower for all the temperatures. Curve (C) shows a surprising result, because if carbon favors chlorination, iron removal should be expected to be higher in this sample, which has an excess of 5% carbon. The excess of carbon in the chlorination of  $\text{Fe}_2\text{O}_3$  favors the reaction, but the final product is  $\text{FeCl}_2$ , which does not volatilize quantitatively up to temperatures close to 900 °C. Lower carbon concentrations kinetically favor the chlorination of  $\text{Fe}_2\text{O}_3$  without creating highly reducing conditions, so that the final product obtained is  $\text{FeCl}_3(\text{g})$ . However, the optimum concentration of carbon can vary, depending on the type of clay and the amount of  $\text{Fe}_2\text{O}_3$  in the mineral.

The lower volatilization of iron in mixtures of pure  $\text{Fe}_2\text{O}_3$  mixed with an excess of carbon and subjected to chlorination has been already experimentally observed (González, 1999; González et al., 2001b). This was attributed in that a carbon excess creates highly reducing conditions, under which the reaction product is  $\text{FeCl}_2$  and not  $\text{FeCl}_3$ . For this to take place, chlorine partial pressure needs to be low, so as to create a deficiency of this reactive gas in the reaction zone. It was observed that this phenomenon was marked in the initial stages of  $\text{Fe}_2\text{O}_3$  carbochlorination; this is to say, at short reaction times and in excess of carbon. These results can be extended to kaolins and clays, and this could clearly account for the experimental data obtained. The reaction is thermodynamically favored and the formation of  $\text{FeCl}_2$  takes place; however, this chloride, unlike  $\text{FeCl}_3$ , starts to volatilize quantitatively in temperatures above 850 °C, and its final concentration in the sample therefore decreases at high temperatures.

Point (D) corresponds to an experiment equivalent to that of curve (B), in which chlorination is performed in a  $\text{Cl}_2$ –air mixture with a  $\text{Cl}_2$  partial pressure of 0.5 atm. The purpose of this experiment was to show that the chlorination of metallic oxides is reversible. Therefore an increase in  $\text{O}_2$  partial pressure unfavors chlorination, as has been already observed in chlorination of other metallic oxides (González et al., 1998a,b,c; González, 1999; González et al., 2001a). The effect of oxygen on the chlorination of ferric oxide has also been reported by other authors, who have observed that  $\text{FeCl}_3$  oxidation with  $\text{O}_2(\text{g})$  gives  $\text{Fe}_2\text{O}_3 + \text{Cl}_2(\text{g})$  as products, in a temperature range similar to that studied here (Wikswó and Nelson, 1967; Dunn, 1975; Dunn, 1982).

The  $\text{TiO}_2$  analyses after chlorination for curves (A), (B) and (C) did not show a quantitative extraction of this element as it occurs with iron, achieving, in a surface analysis, final values similar to those observed in the non-isothermal assays.

The aluminum concentration again showed little changes, except for a slight decrease in samples mixed with carbon and at high temperature. This indicates that at higher temperature and due to the catalytic and reducing effect of carbon, aluminum starts to be extracted from the clay mineral.

The reversibility of chlorination, already demonstrated by the formation of  $\alpha\text{-Al}_2\text{O}_3$ , is another important factor to be considered, then the presence of  $\text{O}_2$  unfavors the chlorination of Fe and Ti oxides. This fact was apparent when a  $\text{Cl}_2$ –air mixture was introduced as reagent gas. The presence of water vapor has an even greater effect than the presence of  $\text{O}_2$ , in the reversibility of the chlorination reaction, especially in refractory oxides, since a more stable product  $\text{HCl}(\text{g})$ , is also obtained. The presence of  $\text{HCl}(\text{g})$  unfavors chlorination, because of its lower chlorinating capacity. For this reason, the introduction of chlorine gas is not recommendable until the clay mineral is not completely dehydrated.

## 5. Conclusions

1. The use of gas chlorine for extraction of iron and titanium from clay minerals has proved to be clearly superior to other physical and chemical procedures, permitting the quantitative extraction of all the iron present in the mineral, including that in the clay crystalline structure.
2. The optimum conditions for quantitative chlorination of iron and partial chlorination of titanium, without aluminum loss, is achieved at temperatures close to  $850\text{ }^\circ\text{C}$ , in controlled atmospheres free of  $\text{O}_2$  and  $\text{H}_2\text{O}$  (g). Besides removing impurities with the consequent whitening of the mineral, chlorination permits to recover the iron and titanium present in the clay.
3. Chlorination makes it possible to extract intra-particle iron, which is considered as nonleachable by other deferrification methods (Cameselle et al., 2003).
4. The presence of carbon favors the chlorination of iron and titanium oxides, due to their thermodynamic and kinetic effects. The content of carbon and organic matter in the clays showed, for the case of the San Luis red clay, to be enough for extraction improvement.
5. The presence of  $\text{O}_2(\text{g})$  unfavors the chlorination of  $\text{Fe}_2\text{O}_3$  due to the reversibility of the chlorination reaction. It is not convenient either to perform iron chlorination in combustion furnaces where  $\text{H}_2\text{O}(\text{g})$  is a reaction product, because the yield of the chlorination will be lower.
6. Even though quantitative extraction of titanium was not achieved, the piece clarity was increased due to the almost total extraction of iron. In this way, the Fe–O–Ti interaction known as “Titania effect”, which reduces the clarity, was prevented.
7. One advantage of chlorination is its application to the whitening of formed ceramic pieces in which it is important not to alter the original properties of the mineral. The technique permits to obtain white pieces even starting from red clays. In this manner, clays which would otherwise be discarded for coloration reasons can be selected according to properties and cost.
8. The phase transformations that chlorine produces in the final product in the studied temperature range are not detrimental for the final piece. On the contrary, the presence of phases such as  $\alpha\text{-Al}_2\text{O}_3$  increases the piece hardness.
9. Some of the mechanisms that intervene in the chlorination of iron and titanium from clays and kaolins can be established by advances in the knowledge on chlorination and its current industrial applications.

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