FIRED PRODUCTS OF Cr-SMECTITE CLAYS IN NITROGEN

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Abstract - The products of Cr-smectite clays heated to 1350 °C in nitrogen were evaluated by X-ray diffraction and chemical analysis. Cr-smectite clays were prepared at room temperature by contact between smectite clays and Cr species contained in OH-Cr solutions. The Cr species were prepared using chromium nitrate solution by addition of NaOH solution with OH/Cr = 2. Products of firing in nitrogen at the high temperature were different (magnesia chromite, donathite, iron chromium oxide and picrochromite) depending on the type of isomorphous substitution of the smectite structure and the amount of retained chromium.
Keywords: Cr-smectite clays in nitrogen, fired products, X-ray diffraction and chemical analysis.

INTRODUCTION

Chromium-smectite clay materials obtained by intercalation of OH-Cr species or Cr cations are used as catalysts and as adsorbents (Carr, 1985; Rengasamy and Oades, 1978; Volzone et al., 1998). The mechanisms by which the chromium clays were obtained, using Cr(III) ions or OH-Cr(III) species from prepared solutions or from wastewater solutions, are explained in several papers (Rengasamy and Oades, 1978; Brindley and Yamanaka, 1979; Pinnavaia et al., 1985; Volzone et al., 1993; Volzone, 1998; Volzone and Tavani, 1995; Tavani and Volzone, 1997). Kaolinites, illites, vermiculites and smectites can be used as clays in order to obtain chromium clays. Some final products obtained from thermally treated chromium clay thermally treated can be suitable for use as materials in the ceramic industries. It is known that the products of the smectite clays fired at high temperature depend on the composition of the clay (Mackenzie and Caillere, 1979). Smectite clays containing different proportions of silicon, aluminum, iron and magnesium, in the layers of the structure and calcium, sodium and potassium as exchangeable cations in interlayer positions result in products such as mullite, cordierite, hematite, anorthite, quartz, etc. after heating at 1000 °C in air (Volzone and Cesio, 1997). On the other hand, the same thermal treatment conditions as those used with smectites treated previously with OH-Cr species gave eskolaite (α-Cr_2O_3) as the only chromium compound. Other phases belonging to each smectite clay were also present. Reinke et al. (1986) observed that the atmosphere during the heating of chromite-magnesia minerals influenced the structural and mineralogical properties of the final refractory products. There is little information on the Cr clays heated in nitrogen at high temperatures. Nevertheless, depending on the products obtained, they may be used in structural ceramic applications.

Smectites are a group of clay minerals. They are 2:1 layer phyllositicates, where two Si^{4+} tetrahedral sheets are separated by one Al^{3+} octahedral sheet.

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Different isomorphic substitutions in the octahedral and tetrahedral sheets result in the members of the smectite clay group (MacEwan and Wilson, 1980) with charge in balance, which is balanced by interlayer cations. There are two different series of smectites, dioctahedral and trioctahedral, according to whether the total number of ions in six-coordination per half unit-cell layer is close to 2.00 or 3.00, respectively.

The aim of this paper is to evaluate the products of the different intercalated chromium-smectite clays heated to 1350 °C in nitrogen.

MATERIALS AND METHODS

The smectites used were beidellite, Taiwan, B; NG-1, nontronite, Germany, N; SapCa-1, saponite, U.S.A., S; and LapRD, synthetic laponite (hectorite), supplied by Laporte Inorganics, L. The structural formulae of the smectites (Table 1) were derived from chemical analyses on the basis of an anion charge of -22 (Volzone and Cesio, 1997).

Hydroxy-chromium (OH-Cr) solution was prepared from 0.1M chromium nitrate solution by addition of 0.2N NaOH (OH/Cr=2) (Volzone, 1997). The smectite water suspension and the hydroxy-chromium solution were stirred and after one day the solid was separated and washed several times with distilled water in order to remove the excess electrolyte. The amount of chromium added was 10 mmol per gram of sample.

For the thermal treatments of the Cr smectites up to 450 °C and 1350 °C a Netzsch STA 409 thermobalance was used. The heating rate was 5 °C min^{-1} and treatment was carried out in nitrogen at a flow rate of 50 ml min^{-1}. After thermal treatment the samples were referred to as Cr smectite X, where smectite is beidellite, nontronite, saponite or laponite and X is the temperature, 450 °C or 1350 °C.

Table 1: Half unit-cell formulae of smectites. (d): dioctahedral smectite; (t): trioctahedral smectite.

Smectite	Tetrahedral sheet		Octahedral sheet				Interlayer			
	Si_{IV}^{4+}	Al_{IV}^{3+}	Al_{VI}^{3+}	Fe^{3+}	Mg^{2+}	Li^+	K^+	Na^+	Ca^{2+}	Mg^{2+}
B(d)	3.61	0.39	1.63	0.11	0.16	0	-	-	0.06	-
N(d)	3.70	0.30	0.13	1.80	0.13	0	0.12	-	0.12	0.22
S(t)	3.82	0.18	0.20	0.02	2.50	0	0.16	0.18	0.10	-
L(t)	4.00	0	0	0	2.77	0.23	0.05	0.02	-	-

The X-ray diffraction (XRD) samples were obtained with an X-ray X´PERT system using the PW3710 Electronic Control Unit with a Philips 3020 goniometer, Cu Kα radiation (λ= 1.5405 Å) at 40 kV and 20 mA and Ni filter by scanning at 1 °(2θ)/min between 3 and 70 °(2θ). The diffractogram of patterns was measured at room temperature on the powder aggregate sample. The d(001) spacing of all samples was measured on oriented slide specimens at room temperature and 55% RH (relative humidity) by scanning at ½° (2θ)/min between 3° and 15° (2θ). To obtain the 55% RH in the samples, the oriented slide was put in a chamber containing a saturated $Ca(NO_3)_2.4H_2O$ solution for one week at room temperature. The chemical composition of the samples was attained by inductively coupled plasma emission spectrometry (ICP).

RESULTS AND DISCUSSION

The Cr solution contained chromium species such as $Cr_n(OH)_m^{3n-m}$ (Volzone, 1997). The species were intercalated in the smectite clay, and as a consequence, the interlayer cations (Ca^{2+}, Na^+, K^+) (Table 1) were replaced by positive chromium species. When the smectites were intercalated, their interlayer spacings increased from 14.9-15.6 Å (smectites: beidellite, nontronite, saponite, laponite) to 16.5-19.6 Å (Cr smectites: Cr beidellite, Cr nontronite, Cr saponite, Cr laponite) (Table 2) and the different value of interlayer separation was attributed to the amount of retained chromium (Volzone, 2001). Table 1 shows the composition of the saturation interlayer cations (K^+, Na^+, Ca^{2+}, Mg^{2+}) which define the different d(001) spacings of

the smectite clays (MacEwan and Wilson, 1980). Table 2 shows how these spacings were influenced by the interaction of OH Cr species and also how the atmosphere influenced the thermal treatment. When the Cr smectites were heated at around 450 °C in air, α-Cr_2O_3 appeared (exothermic peak in differential thermal analysis, Volzone and Cesio, 1997, confirmed by X-ray diffraction) and the d(001) spacing decreased to 9.9-15.5 Å (Cr smectites 450/air) (Table 2). The collapsed value for Cr nontronite 450/air was associated with dehydroxylation of the 2:1 layer of nontronite that occurs at close to 490 °C (Mackenzie and Caillere,

1979; Volzone and Cesio, 1997). When the same Cr smectites were heated in nitrogen at 450 °C, the α-Cr_2O_3 phase did not appear (no exothermic peak in DTA, as shown in Figure 1) and the d(001) spacings were higher than in air and the values were in the range of 13.8-17.7 Å (Cr smectites 450/nitrogen) (Table 2). This spacing is produced by some kind of cationic chromium species in the interlayer as pillaring. This type of materials is generally called PILCs (pillared clays), which show textural and acidity characteristics that could enable their use as adsorbents or in catalysis (Pinnavaia et al., 1985; Volzone, 2001).

Table 2: d(001) spacing of the smectites under different conditions.

Sample	d(001), Å
Beidellite	14.9
Cr beidellite	16.5
Cr beidellite 450/air	14.7
Cr beidellite 450/nitrogen	15.8
Nontronite	15.6
Cr nontronite	16.2
Cr nontronite 450/air	9.9
Cr nontronite 450/nitrogen	13.8
Saponite	15.2
Cr saponite	17.1
Cr saponite 450/air	15.0
Cr saponite 450/nitrogen	15.2
Laponite	broad
Cr laponite	19.6
Cr laponite 450/air	15.5
Cr laponite 450/nitrogen	17.7
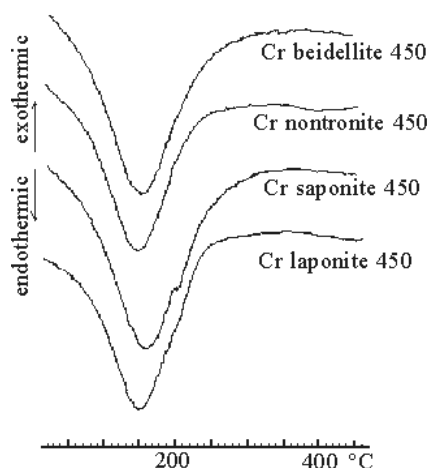
Figure 1: Differential thermal analysis curves for Cr smectites
heated up to 450 °C in nitrogen.

Detailed analyses of XRD diagrams of the fired products of Cr smectites in nitrogen were done and the results are shown in Figures 2-5.

The fired products of the Cr beidellite 1350 are shown in Figure 2. Due to the considerable amount of amorphous products, the XRD scanning (smooth and magnification) was improved, as shown in the same figure. The phases in this sample were magnesiochromite, $(Mg,Fe)O.(Al,Cr)_2O_3$; spinel, $MgO.Al_2O_3$; mullite/sillimanite, $3Al_2O_3.2SiO_2/Al_2O_3.SiO_2$; SiO_2 as quartz and amorphous material. Since the major element of Cr beidellite was aluminum (Table 3), which came from raw smectite, mullite/sillimanite and spinel were the principal compounds. Some of the principal spacings of mullite and sillimanite patterns were not in complete agreement with the powder diffractogram file (Brown, 1980). The iron content in Cr nontronite produced donathite, $(Fe,Mg)O.(Cr,Fe)_2O_3$, and also

chromite iron, $FeO.(Cr,Al)_2O_3$, at the high temperature (Cr nontronite 1350) (Figure 3). Cristobalite and quartz plus amorphous products were also found in this fired sample.

Cr saponite and Cr laponite contain high percentages of magnesium (Table 3), then clinoenstatite and enstatite, $MgO.SiO_2$, respectively, were the main phases in those samples (Cr saponite 1350, Figures 4, and Cr laponite 1350, Figure 5). On the other hand, chromium was present as magnesiochromite $(Mg,Fe)O.(Al,Cr)_2O_3$ and $MgO.Cr_2O_3$ (picrochromite) in the heated Cr saponite and Cr laponite, respectively. Peaks that could correspond to cristobalite were also found. The aluminum contained in saponite (Table 3) produced spinel, $MgO.Al_2O_3$. No phases containing lithium were found by XRD in Cr laponite 1350. A low content of lithium silicate is probably present but overlapped in the range of 18 to 33 ° (2θ) in the XRD diagram (Figure 5).
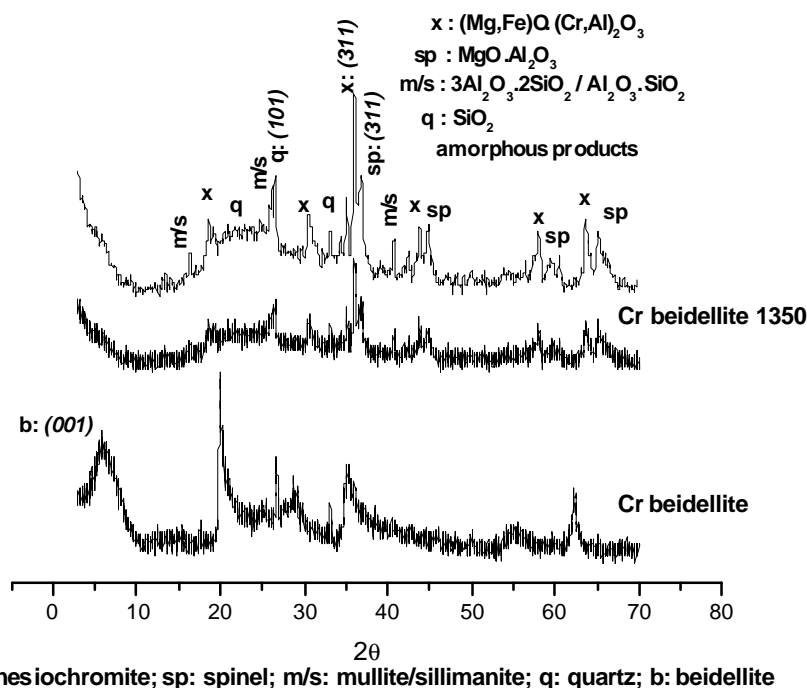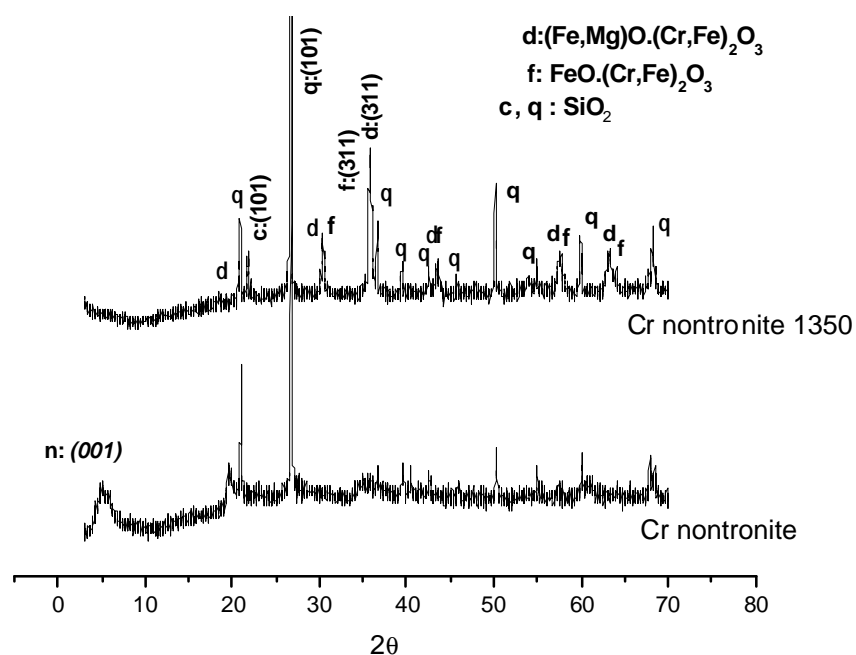

Figure 2: XRD patterns of Cr beidellite, both unfired and fired at 1350 °C in nitrogen.

Table 3: Elements of smectite structure after chromium treatment, in mmol.

Cr smectite	Si^{4+}	Al^{3+}	$Fe^{2+/3+}$	Mg^{2+}	Li^+	Cr^{3+}
Cr beidellite	679.0	176.0	20.0	38.0	0	65.0
Cr nontronite	878.0	48.0	96.0	5.0	0	56.0
Cr saponite	620.0	32.0	4.0	455.0	0	85.0
Cr laponite	667.0	0	0	367.0	45	90.0

d: donathite; f: iron chromium oxide; q: quartz; c: cristobalite; n: nontronite

Figure 3: XRD patterns of Cr nontronite, both unfired and fired at 1350 °C in nitrogen.

Table 4: Products after firing Cr smectite clays at 1350 °C in nitrogen.

	Products obtained in nitrogen	
Cr beidellite 1350	(Mg, Fe)O.(Cr,Al)$_2$O$_3$ magnesiochromite	13.0 %
	MgO.Al$_2$O$_3$ spinel	4.5 %
	3Al$_2$O$_3$.2SiO$_2$, mullite/Al$_2$O$_3$.SiO$_2$, sillimanite	14.8 %
	SiO$_2$ as quartz + amorphous	66.7 %
Cr nontronite 1350	(Fe, Mg)O.(Cr,Fe)$_2$O$_3$ donathite	13.0 %
	FeO.(Cr,Al)$_2$O$_3$ iron chromium oxide	8.3 %
	SiO$_2$ as quartz and cristobalite + amorphous	67.0 %
Cr saponite 1350	(Mg,Fe)O.(Cr,Al)$_2$O$_3$ magnesiochromite	37.5 %
	MgO.Al$_2$O$_3$ spinel	2.8 %
	MgO.SiO$_2$ clinoenstatite	44.9 %
	SiO$_2$ cristobalite	14.8 %
Cr laponite 1350	MgO.Cr$_2$O$_3$ picrocromite (magnesiochromite)	12.9 %
	MgO.SiO$_2$ enstatite	56.0 %
	SiO$_2$ cristobalite	20.7 %

The chemical compositions of the Cr smectite clays are shown in Table 3. The amount of retained chromium was different for each smectite clay, and according to a previous paper, the retention of chromium by natural clays is a function of the number of charges in octahedral positions in the structure (Volzone, 1998). Taking into account the chemical composition of each Cr-smectite clay (Table 3) and the results of the XRD patterns, it was possible to estimate the relative composition of the present phases (Table 4). The relative percentages of Cr phases at high temperature were in the range of 13-37 %, depending on the original type of smectite and chromium retained. Contrary to what was found in Cr smectites fired in air at 1000 °C (Volzone and Cesio, 1997) no α-Cr$_2$O$_3$ was detected in our fired products.
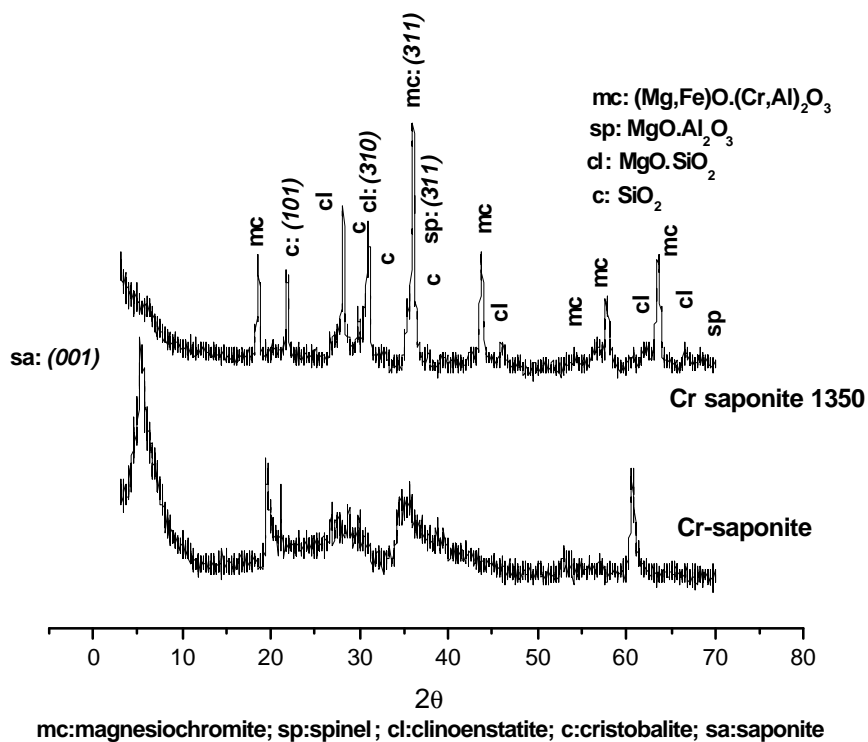
Figure 4: XRD patterns of Cr saponite, both unfired and fired at 1350 °C in nitrogen.
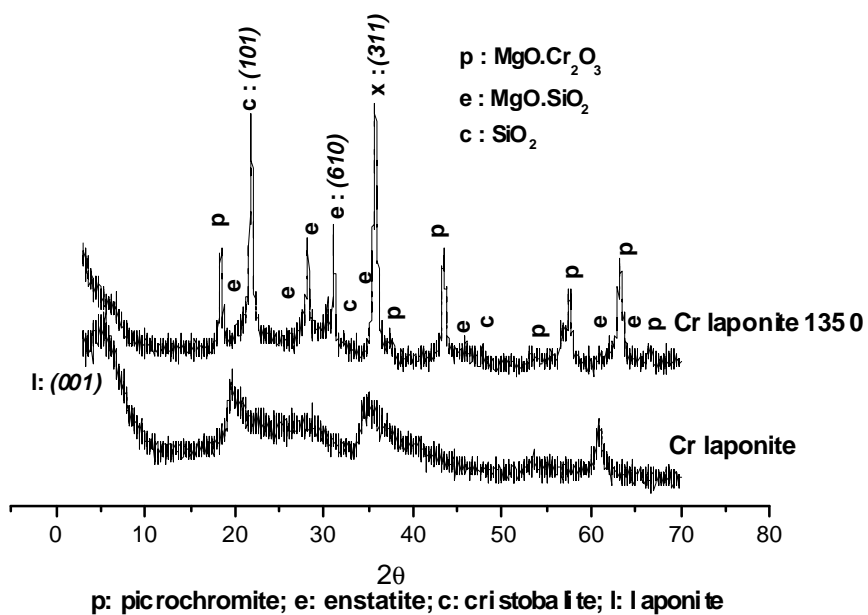

Figure 5: XRD patterns of Cr laponite, both unfired and fired at 1350 °C in nitrogen.

CONCLUSIONS

The original composition of smectite clays and retained chromium influenced the kind of products obtained at 1350 °C in nitrogen.

The chromium products obtained by heating to 1350 °C in nitrogen of the chromium-intercalated smectites, range from magnesio-chromium oxides, which contain Al and Fe, to picrochromite $MgO.Cr_2O_3$. Heating under these conditions, applied to intercalated clays with chromium from polymeric solutions or from wastewater, would result in similar potential industrial products.

The α-Cr_2O_3 phase that was found in Cr-smectite clays heated in air up to 1000 °C (Volzone and Cesio, 1997) was not found in the same Cr-smectite clays fired in nitrogen.

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