

A NEW EXTRACTION PROCEDURE FOR SIMULTANEOUS QUANTITATIVE DETERMINATION OF WATER-SOLUBLE METALS IN REACTION PRODUCTS OF CLAYS AND INORGANIC SALTS

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Abstract—Kaolin, a possible source of Al, may be reacted with inorganic acids or salts to form different Al salts that can be further processed to prepare metallic Al. Although the reaction of kaolin and acid in aqueous solution can be monitored by chemical analysis of Al, the Al salts must be extracted from any unreacted kaolinite. Also, the lixiviation of Ti or Fe species present in kaolin should be monitored. A simple extraction procedure is reported to determine, quickly and quantitatively, water-soluble Al, Ti and Fe metals present in products of reaction of kaolin (85 wt.% kaolinite, 12 wt.% mica, 2 wt.% feldspar, 1 wt.% quartz) with inorganic salts, such as sodium hydrogensulfate, using conventional glassware for the glass reaction tubes. Optimum results are obtained with 250 mL glass reaction tubes. The best operating conditions found for this piece of equipment are: (1) sample weight of 0.05 g, (2) lixiviation time of 1 h, and (3) lixiviating agent, 50 mL of an aqueous solution of pH = 1 H₂SO₄ at its boiling point. Comparisons are made with soxhlet extraction and beaker and magnetic stirring methods.

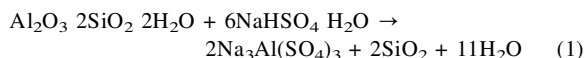
Key Words—Inorganic Salt Reaction, Kaolin, Water-soluble Metal Determination.

INTRODUCTION

Aluminum is usually produced from bauxite and many countries are dependent upon foreign sources for its supply, as bauxite is not widely distributed around the world (Ruiz, 1988). Therefore, alternative sources of Al are being sought. Kaolin is an economic source of Al as it is an abundant and widespread Al-rich mineral. Many papers describe processes to produce Al from kaolin by using different reactions. Usually, these methods involve suspending kaolin in a water solution of an inorganic acid (HCl, H₂SO₄, HNO₃) to render Al and other metals soluble (Ford, 1992; Hulbert and Huff, 1970; Ziegenbalg and Haake, 1983). Other methods use inorganic salts such as (NH₄)₂SO₄, NH₄H₂SO₄ (Bayer *et al.*, 1982; Davies *et al.*, 1945; Fetterman and Sun, 1963; Fouda *et al.*, 1993; Nagaishi *et al.*, 1982; Peters *et al.*, 1965; Seyfried, 1949; St. Clair *et al.*, 1944), or NaHSO₄ (Garcia-Clavel *et al.*, 1979, 1982, 1983, 1985; Martinez-Lope *et al.*, 1991; Solano and Juan, 1995) that are calcined with kaolin to produce mixtures of Al sulfates and/or Na-Al sulfates together with unreacted kaolin. Afterwards, the extraction is completed using a hot, acidic aqueous solution that leaches the reacted salt/kaolin mixture to produce Al and other metals soluble in water. This solution is processed further to obtain a pure Al salt from which to produce pure metallic Al.

Several papers (Heller-Kallai, 1978; Heller-Kallai and Frenkel, 1979; Peters *et al.*, 1963) describe the reaction between kaolin and inorganic salts. The reaction with Na hydrogensulfate has also been reported as a

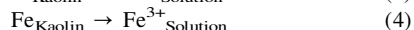
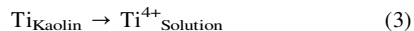
means of obtaining soluble Al salts from kaolin (Garcia-Clavel *et al.*, 1979, 1982, 1983, 1985; Martinez-Lope *et al.*, 1991; Solano and Juan, 1995). According to Martinez-Lope *et al.* (1991) the reaction is described by the equation:



For the purpose of the present work it is considered as:



The reaction between kaolin and Na hydrogensulfate also solubilizes impurities, *e.g.* Ti (Dolcater *et al.*, 1970; Maynard *et al.*, 1969) and Fe (Malden and Meads, 1967). Similar to Al, the solubilization of Ti and Fe can be described by the following reactions:



According to equations 2, 3 and 4, the reaction yield is defined as:

$$X_M = \frac{n_{M(\text{kaolin}0)} - n_{(\text{kaolin})}}{n_{M(\text{kaolin}0)}} \quad (5)$$

where $n_{M(\text{kaolin}0)}$ is the initial number of moles of M (where $M = \text{Al}, \text{Ti}$ or Fe) in unreacted kaolin, expressed as moles of the corresponding oxide, and $n_{M(\text{kaolin})}$ is the number of moles of M in reacted kaolin, also expressed as the oxide.

These reactions have been discussed by many (Bayer *et al.*, 1982; Fouda *et al.*, 1993; Garcia-Clavel *et al.*, 1979, 1982, 1983, 1985; Martinez-Lope *et al.*, 1991; Nagaishi *et al.*, 1982; Peters *et al.*, 1963, 1965; Seyfried, 1949; Solano and Juan, 1995), but none has shown an

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extraction procedure that produces fast and reproducible results for soluble metals. Sample reactions can be performed quickly, but chemical analysis of the products is time consuming and involves not only the determination of the concentration of Al and other species present in the lixiviate, but also the quantitative extraction of the soluble salts obtained as products as well.

A good methodology is to be selective, determining only soluble products of the reaction, leaving aside non-soluble products of reaction and the Al present in the unreacted kaolin. Ideally, the methodology involves small sample weights, used frequently in kinetic studies. Such small amounts of sample are usually generated to ensure that thermal equilibrium is achieved quickly, because temperature is a crucial variable in the study of kinetics. In this paper, three extraction methods to isolate soluble Al, Ti and Fe from mixtures of reacted Na hydrogensulfate and kaolin are compared. The advantages and disadvantages are discussed and a new procedure is proposed.

MATERIALS AND METHODS

Kaolin (Remblend grade) from St. Austell, Cornwall (UK) was supplied by English China Clays International Europe Ltd. (St. Austell, UK). Mineralogical analysis (Chung, 1974) of the kaolin was performed on a D-500 Siemens X-ray diffractometer, indicating 85 wt.% kaolinite, 12 wt.% mica, 1 wt.% quartz, and 2 wt.% feldspar. The Hinckley index (HI) (Hinckley, 1963) for the kaolin sample was 1.07. Major elements were determined by X-ray fluorescence (XRF) analysis of fused material using lithium tetraborate as the flux. The analysis was performed on a PW 1400 Philips spectrophotometer, using a Rh anode tube. Trace elements were determined by inductively coupled plasma-optical emission spectroscopy (ICP-OES) using a Polyscan 61E Thermo Jarrell Ash spectrophotometer. All reagents were Baker Analyzed, analytical grade (J.T. Baker Chemicals N.V. Deventer, Holland). Results of the chemical analysis of the kaolin are given in Table 1. Particle-size distribution was measured by light scattering using a Microtrac SRA150 from Leeds & Northrup. The analysis shows an average diameter of 15 μm .

A standard Na salt of analytical grade supplied by Probus (Barcelona, Spain) was used as a reagent. Qualitative X-ray diffraction analysis showed that it was mostly $\text{NaHSO}_4 \cdot \text{H}_2\text{O}$, with minor amounts of the anhydrous salt. The NaHSO_4 was ground before reacting with kaolin to obtain salt particles of the same size as kaolin particles. Chemical analysis of Na hydrogensulfate after grinding gave 0.002 wt.% in Fe and 0.001 wt.% in heavy metals (expressed as Pb), indicating that no significant amounts of the species came from the salt.

Samples for lixiviation tests were prepared by reaction of kaolin rock with Na hydrogensulfate.

Reactions were undertaken by mixing kaolin and freshly molten Na hydrogensulfate in a molar ratio of 6:1 according to equation 1. Aliquots of the mixture were placed in Haldenwanger 79C-3 porcelain crucibles, which were heated in a 10-PR/300 Heron furnace using a flash procedure to a temperature of $400 \pm 5^\circ\text{C}$. The heating rate of the sample was $1-5^\circ\text{C/s}$. Once the reaction temperature was reached, the crucibles were left in the furnace for 1 h. After the reaction time elapsed, the crucibles were removed from the furnace, cooled in air, the samples removed, and ground using a mortar and pestle. Intensive grinding was avoided to limit metal extraction of the clay itself which can solubilize some metals by mechanical activation (Kletsov *et al.*, 1988; Ruiz, 1988). The reaction temperature of 400°C and reaction time of 1 h were shown to produce reasonable reaction yields for the purpose of the present work (Martinez-Lope *et al.*, 1991; Colina, 1999).

The mineralogical analysis of reacted samples was performed on a D-500 Siemens X-ray diffractometer using $\text{CuK}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). Diffraction patterns were recorded between 4 and 70° with a step size of 0.05° . Patterns were compared to the Powder Diffraction File database of the International Centre for Diffraction Data (PDF-ICDD). Diffraction patterns of reacted samples showed unreacted kaolin and soluble Al salts, such as $\text{Na}_3\text{Al}(\text{SO}_4)_3$, as previously reported by Martinez-Lope *et al.* (1991) and Colina (1999).

For the purposes of the present work, lixiviation tests were performed using three different apparatus: (1) soxhlet; (2) beaker and magnetic stirrer; and (3) glass reaction tube with condenser (Figure 1). As discussed below, three parameters were considered: (1) sample weight; (2) lixiviation time; and (3) volume of lixiviating agent. Two additional parameters, the nature of lixiviating agent and the pH of lixiviating solution, were only considered for reaction tubes. In any case, the temperature of the lixiviating agent was

Table 1. Chemical analysis of kaolin.

Major elements		Trace materials	
Component	Wt.%	Component	ppm
SiO_2	47.02	Na_2O	960
Al_2O_3	36.81	C	700
Fe_2O_3	1.05	S	600
TiO_2	0.11	CaO	600
K_2O	1.90	Ba	267
MgO	0.28	Rb	241
P_2O_5	0.15	Sr	153
		Zr	104
		MnO	100
		Y	32
LOI ¹	11.96	Th	28
Total	100.7	Pb	18
		Nb	16
Moisture	8	Cr	7

¹ Loss on ignition

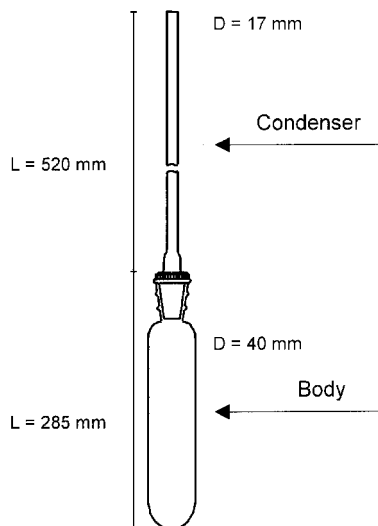


Figure 1. Reaction tube used in the lixiviation method, showing body and condenser (L: length; D: diameter).

maintained at its boiling point, which was $>100^{\circ}\text{C}$, and sufficient to render all the metals soluble in a short period.

The soxhlet used in the present work was of the standard 250 mL type. Samples (5 g) were introduced into the soxhlet using cylindrical filters and 200 mL of aqueous solution of $\text{pH} = 1$ H_2SO_4 were added. The system was left at its boiling point for 1–5 h, depending on the experiment. Once the time had elapsed, the liquid was filtered and transferred into 250 mL volumetric flasks. Aliquots were taken for chemical analysis.

In the case of the beaker and magnetic stirrer, standard 250 mL beakers were used. Depending on the experiment, 0.05 g to 1 g of sample were dropped into the beaker, together with 25–50 mL of aqueous solution of $\text{pH} = 1$ H_2SO_4 . Magnetic stirring and heating were switched on, and the system was left at its boiling point for 1–2 h, depending on the experiment. To avoid losses, the beakers were always covered with watch glasses. Once the time had elapsed, the liquid was filtered and transferred into 100 mL volumetric flasks. Aliquots were taken for chemical analysis.

In the case of glass reaction tubes, 250 mL reaction tubes were used. Depending on the experiment, 0.05–0.10 g of sample were placed in the bottom of the reaction tube. Depending on the experiment, 25–50 mL of aqueous solution of H_2SO_4 ($\text{pH} = 1$) were added, the condenser mounted, and the system was inserted into an Al block heater. The system was left at its boiling point for 1–2 h, depending on the experiment and then the liquid was filtered and transferred into 100 mL volumetric flasks. Aliquots were taken for chemical analysis.

Chemical analysis of reagents and metals present in lixiviates was performed by ICP-OES as described above

for clay. Lixivate concentrations of Al, Ti and Fe were measured for each sample. A blank was prepared by calcining kaolin in the porcelain crucible at $400 \pm 5^{\circ}\text{C}$ for 1 h. As the extraction method can leach some Al, Ti and Fe from unreacted kaolin, the Al, Ti and Fe values obtained from this analysis were subtracted from those obtained in the analysis of samples of reaction of kaolin with the salt. Reaction yields obtained for the blank were always lower than the standard deviations for the reacted samples (0.0003 for Al, 0.0001 for Ti and 0.0001 for Fe expressed in moles of the corresponding oxide). Each experiment was performed at least three times.

Standards used in ICP-OES were supplied by J.T. Baker Chemicals N.V. (Deventer, Holland), Union Chimique Belge (Brussels, Belgium) and Aldrich (Milwaukee, Wisconsin, USA) and were checked by ICP-OES analysis using 1000 ppm standards from Johnson Matthey-Alfa GmbH (Karlsruhe, Germany). Water used in this work was MilliQ quality (conductivity value >18 Mohms cm).

RESULTS AND DISCUSSION

The soxhlet method gave good extraction results (Table 2), though not without some problems: (1) it took a long time to perform the extraction, because of the low volatility of water (4.5 h per sample); (2) large sample weights (5 g) were needed for extraction; (3) leached solid eventually passed through the standard soxhlet filters; and (4) the transfer of the lixiviate after extraction was difficult. Nevertheless, the results obtained using soxhlet extraction were of the same order of magnitude as other techniques and may be considered representative. However, standard deviations were high. Because extractions performed with the soxhlet were excessively time consuming and required sample sizes which are often not available, no further tests were performed.

The beaker and magnetic stirring method allows the solubilization of the Al salts. However, the metal concentrations determined showed low reproducibility and the standard deviations were the largest for any method. The beaker method allows the use of small amounts of sample and a simple and effective transfer of lixiviate solution. The low reproducibility was related to water losses in vapor form, although beakers were covered with watch glasses. Moreover, irregular shaking of the suspended solids and liquid by the magnetic stirrer may also be a source of error.

When glass reaction tubes were used, the sample weight affected both the reproducibility of the results and the lixiviating effectiveness of the equipment. A large sample weight makes the analysis more reliable, though time consuming. In contrast, a small sample weight requires careful homogenizing of the sample prior to analysis, but lixiviation can be achieved rapidly. Good results were obtained (Table 2) with sample

Table 2. Results of lixiviation tests.

No.	Method	Sample weight (g)	Lixiviate time (h)	Amount of solvent (mL)	Yields (moles)		
					X_{Al}	X_{Ti}	X_{Fe}
1	Soxhlet	5.00	4.5	200	0.168 (5)	0.029 (2)	0.064 (3)
2	Beaker	0.10	1.0	25	0.20 (1)	0.03 (1)	0.14 (2)
3	Beaker	0.10	1.0	50	0.21 (2)	0.04 (1)	0.16 (2)
4	Beaker	0.10	2.0	25	0.18 (2)	0.02 (1)	0.23 (1)
5	Beaker	0.10	2.0	50	0.21 (3)	0.04 (1)	0.14 (2)
6	Beaker	0.05	2.0	50	0.21 (2)	0.04 (1)	0.14 (1)
7	Reaction tube	0.10	1.0	25	0.198 (5)	0.016 (4)	0.128 (3)
8	Reaction tube	0.10	1.0	50	0.209 (3)	0.023 (1)	0.142 (2)
9	Reaction tube	0.10	2.0	25	0.212 (3)	0.029 (3)	0.135 (3)
10	Reaction tube	0.10	2.0	50	0.210 (5)	0.027 (5)	0.145 (3)
11	Reaction tube	0.05	1.0	25	0.212 (5)	0.021 (4)	0.139 (4)
12	Reaction tube	0.05	1.0	50	0.221 (2)	0.030 (3)	0.187 (2)
13	Reaction tube	0.05	2.0	25	0.218 (4)	0.031 (2)	0.143 (1)
14	Reaction tube	0.05	2.0	50	0.203 (8)	0.035 (6)	0.133 (3)

weights as low as 0.05 g, but results obtained using 0.025 g were poor (not shown). Thus, the best sample weight when reaction tubes are used is 0.05 g. Actually, sample weights of 0.05 g could be processed in both the beaker and reaction tube methods, but the reaction tube method prevents water loss effectively.

Experiments performed in glass reaction tubes with differing lixiviation times (Table 2) showed that experiment times of either 1 or 2 h produced acceptable results.

The volume of the lixiviating agent is directly related to the size of the reaction tubes (250 mL for the present study) and to the expected concentration of soluble Al salts. The volume of lixiviating agent must be sufficient to allow complete dissolution of soluble salts present in the sample, but sufficiently low to avoid unnecessary dilution of the species to be analyzed. Experiments 5 and 6 (Table 2) show that the volumes tested (25 and 50 mL) are both acceptable, but practice showed that using 50 mL of lixiviating agent was more convenient for transfer of liquids for analytical purposes.

Four inorganic acids were considered as lixiviating agents in the glass reaction tubes method: H_2SO_4 , HCl, HNO_3 and $HClO_4$. Of these, H_2SO_4 was found to be most suitable as it has low volatility and it does not form insoluble salts with Al, Ti and Fe. HCl requires adaptation of the equipment to avoid loss of gaseous HCl. HNO_3 can be used also, but its oxidizing properties may cause the formation of insoluble TiO_2 . $HClO_4$ may be hazardous and requires specially-designed fume

hoods, and thus was not investigated. H_2SO_4 and HCl were considered in detail (Table 3). Lixiviation tests were performed at pH = 1. Reaction yields are slightly higher for HCl because of the formation of chloride compounds such as $AlCl_3$. This is consistent with the results reported by Hulbert and Huff (1970) on the effect of the anion of the acid on the reaction yield, to give higher yields for HCl. Results for Ti and Fe yields show bigger differences, perhaps owing to their lower initial concentration. However, the difference in Al yield obtained through HCl or H_2SO_4 , though significant, is small so that both acids may be considered equally good lixiviation solutes. Whether HCl or H_2SO_4 should be used depends on the composition of the sample to be analyzed. For example, when organic matter is present in the sample, hydrochloric acid is better. For the present case, sulfuric acid was preferred because of its lower volatility.

Experiments were performed in reaction tubes under various pH conditions, obtained by adding H_2SO_4 or NaOH. Figure 2 shows that the maximum yields are obtained in the pH interval of -1 to 1. No significant differences in Al, Ti and Fe yields were observed until pH levels reached the value of 2. Titanium yields are lower at pH values of ≥ 2 . Thus, the best pH values are in the interval of -1 to 1.

CONCLUSIONS

Lixiviation in reaction tubes is a reliable method to extract water-soluble metals in products of reaction of kaolin with inorganic salts. Although not tested, the method can probably also be successfully applied to the analysis of water-soluble metals in products of reaction of kaolin with other inorganic salts such as ammonium sulfates.

The use of this procedure for samples of kaolin with large amounts of Ti and Fe minerals could give misleading results, and it would be advisable to fine

Table 3. Al, Ti and Fe reaction yields (X , in moles) at pH = 1 using different acids (standard deviation in brackets).

Acid	X_{Al}	X_{Ti}	X_{Fe}
HCl	0.227 (3)	0.071 (4)	0.160 (3)
H_2SO_4	0.221 (2)	0.030 (3)	0.187 (2)

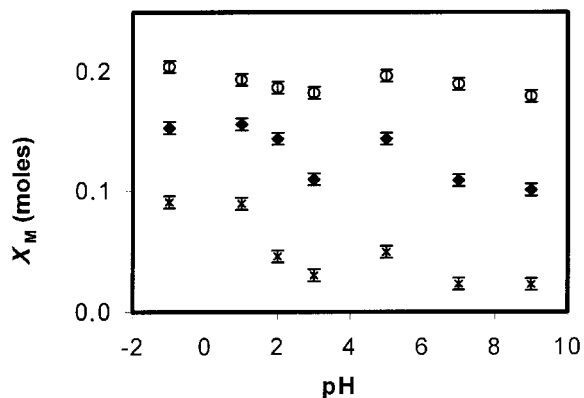


Figure 2. Relationship between Al (□), Fe (●) and Ti (■) yields and pH of solvent (results are calculated as mole % of the corresponding oxide).

tune the described procedure for such a sample. Regarding organic matter, it is usually lost as CO_2 during reaction. Other sources of temperature-resistant organic matter, should they exist, would need to be taken into consideration. In such cases, HCl should be used in preference to H_2SO_4 .

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REFERENCES

- Bayer, G., Kahr, G. and Mueller-Vonmoos, M. (1982) Reactions of ammonium sulphates with kaolinite and other silicate and oxide minerals. *Clay Minerals*, **17**, 271–283.
- Chung, F.H. (1974) Quantitative interpretation of X-ray diffraction patterns of mixtures. I. Matrix flushing method for quantitative multicomponent analysis. *Journal of Applied Crystallography*, **7**, 519–525.
- Colina, F.G. (1999) Procesos industriales de acondicionamiento de caolín para su utilización como materia prima en la síntesis de zeolita X. PhD dissertation. Department of Chemical Engineering and Metallurgy, Universitat de Barcelona, Spain, 382 pp.
- Davies, H., Dering, H.O. and Parker, T.W. (1945) Al_2O_3 from clay by an NH_4 alum- NH_3 process. U.S. Patent no. 2,375,977.
- Dolcater, D.L., Syers, J.K. and Jackson, M.L. (1970) Titanium as free oxide and substituted forms in kaolinites and other soil minerals. *Clays and Clay Minerals*, **18**, 71–79.
- Fetterman, J.W. and Sun, S.C. (1963) Alumina extraction from a Pennsylvania diasporic clay by an ammonium sulfate process. *Alumina*, **1**, 333–349.
- Ford, K.J.R. (1992) Leaching of fine and pelletised Natal kaolin using sulphuric acid. *Hydrometallurgy*, **29**, 109–130.
- Fouda, M.F.R., Amin, R.S. and Abd-Elzaher, M.M. (1993) Characterization of products of interaction between kaolin ore and ammonium sulphate. *Journal of Chemical Technology and Biotechnology*, **56**, 195–202.
- García-Clavel, M.E., Martínez-Lope, M.J. and Casais-Alvarez, M.T. (1979) Método de obtención de alúmina a partir de arcillas y silicatos aluminicos en general. Spanish Patent no. 482.881.
- García-Clavel, M.E., Martínez-Lope, M.J. and Casais-Alvarez, M.T. (1982) Method for obtaining alumina from clays. U.S. Patent no. 4,342,729.
- García-Clavel, M.E., Martínez-Lope, M.J. and Casais-Alvarez, M.T. (1983) Procedimiento continuo de obtención de compuestos de aluminio a partir de silicatos aluminicos y otros minerales de aluminio. Spanish Patent no. 522.398.
- García-Clavel, M.E., Martínez-Lope, M.J. and Casais-Alvarez, M.T. (1985) Método de solubilización de los componentes metálicos de los filosilicatos. Spanish Patent no. 545.690.
- Heller-Kallai, L. (1978) Reactions of salts with kaolinite at elevated temperatures. I. *Clay Minerals*, **13**, 221–235.
- Heller-Kallai, L. and Frenkel, M. (1979) Reactions of salts with kaolinite at elevated temperatures. II. *Developments in Sedimentology*, **27**, 629–637.
- Hinckley, D.N. (1963) Variability in crystallinity values among the kaolin deposits of the coastal plain of Georgia and South Carolina. *Clays and Clay Minerals*, **11**, 229–235.
- Hulbert, S.F. and Huff, D.E. (1970) Kinetics of alumina removal from a calcined kaolin with nitric, sulphuric and hydrochloric acids. *Clay Minerals*, **8**, 337–345.
- Klevtsov, D.P., Logvinenko, V.A., Zolotovskii, B.P., Krivoruchko, O.P. and Buyanov, R.A. (1988) Kinetics of kaolinite dehydration and its dependence on mechanochemical activation. *Journal of Thermal Analysis*, **33**, 531–535.
- Malden, P.J. and Meads, R.E. (1967) Substitution by iron in kaolinite. *Nature*, **215**, 844–846.
- Martínez-Lope, M., García-Clavel, M.E. and Casais-Alvarez, M.T. (1991) Solubilization reaction of the alumina from kaolin by solid state reaction. *Thermochemica Acta*, **177**, 77–82.
- Maynard, R.N., Millman, N. and Iannicelli, J. (1969) A method for removing titanium dioxide impurities from kaolin. *Clays and Clay Minerals*, **17**, 59–62.
- Nagaishi, T., Ishiyama, S., Yoshimura, J., Matsumoto, M. and Yoshinaga, S. (1982) Reaction of ammonium sulphate with aluminium oxide. *Journal of Thermal Analysis*, **23**, 201–207.
- Peters, F.A., Johnson, W. and Kirby, R.C. (1963) Methods for producing alumina from clay: An evaluation of a potassium alum process. U.S. Department of the Interior, Bureau of Mines, Report of Investigations RI 6290.
- Peters, F.A., Johnson, P.W. and Kirby, R.C. (1965) *Methods for producing alumina from clay: An evaluation of two ammonium alum processes*. US Department of the Interior, Bureau of Mines, Report of Investigations RI 6573.
- Ruiz, M.T. (1988) Obtención de alúmina por ataque ácido de materiales no bauxíticos españoles activados por aportación de energía mecánica. PhD dissertation. Departamento de Química Inorgánica, Universidad de Sevilla, Spain, 355 pp.
- Seyfried, W.R. (1949) The ammonium sulfate process for the extraction of alumina from clay and its application in a plant in Salem, Oregon. *Transactions of AIME*, **182**, 39.
- Solano, E. and Juan, D. (1995) Obtención de alúmina a partir de arcillas utilizando como agente disgregante el bisulfato sódico. *Química e Industria*, **14**, 82–85.
- St. Clair, H.W., Ravitz, S.F., Sweet, A.T. and Plummer, C.E. (1944) The ammonium sulfate process for production of alumina from western clays. *Transactions of AIME*, **159**, 255–256.
- Ziegenbalg, S. and Haake, G. (1983) Investigations into the alumina extraction from clay by hydrochloric and sulphuric acid leaching. *Light Metals*, 1119–1143.

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