

Zeolite Synthesis Employing Alkaline Waste Effluents from the Aluminum Industry

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Zeolites 4A, 13X, Y, and HZSM5 have been synthesized from alkaline residues from aluminum finishing plants. These residues could contain concentrations of sodium aluminate and sodium hydroxide between 200 and 300 Kg/m³, and small concentrations of heavy metal cations (Cd, Co, Cr, Cu, Mn, and Zn). These contaminants make handling and disposal of these residues difficult.

However, the physico-chemical properties of the synthesized zeolites (cation exchange capacity of 3 mmol g⁻¹, specific surface area between 600-900 m²g⁻¹, particle size distribution between 0.5-2 μm and whiteness of 97%) make them useful as detergents and catalysts.

Analysis of the chemical composition of the raw materials and the reaction products demonstrates that the heavy metal cation content in the synthesized zeolites is low enough to allow their industrial use (lower than that of the original residues). Therefore, the production of various types of zeolites for industrial use could be used for the elimination of these residues from the aluminum industry.

INTRODUCTION

In the anodized aluminum industry, large quantities of residues in the form of sludge and liquid effluents are produced from cleaning operations. The large volume of these waste products, and the increasing costs for their disposal discourage development of new anodizing facilities, especially when considering that this sector, in general, is comprised of small- and medium-sized companies.

In anodizing or coating plants, the rolled and extruded products are first surface cleaned to elimi-

nate greasy oxide deposits and other impurities. These operations employ sodium hydroxide solutions with concentrations between 50 to 200 Kg/m³, at temperatures of 50 to 60° C, to dissolve the aluminum surface to form sodium aluminate. Periodic regeneration of the caustic bath and elimination of the residues is necessary.

In 1999, 190 million m² of anodized aluminum and 368 million m² of coated aluminum were produced in Europe [1], equivalent to a total of 1.55 million tons. Production of 1.63 and 1.67 million tons for the years 2000 and 2001, respectively, has been predicted. Allowing for an average aluminum loss of 2 to 4 g per m² of treated surface, and the necessity to regenerate the pickling bath when the sodium aluminate concentrations are greater than 200 Kg/m³, it can be estimated that, in Europe in 1999, approximately 26,000 m³ of residues were produced. In the year 2001, this was approximately 27,000 m³.

Aluminum profiles are fabricated by hot extrusion (450 to 470° C). In order to achieve good quality products, perfect cleanliness of the internal surfaces of the extruder matrixes is essential [2]. To maintain the cleanliness of the matrixes, they are regularly dismounted and treated in a concentrated hot (100° C) sodium hydroxide cleaning bath. Generally, this operation is performed after 3,000 Kg of aluminum have been extruded, with an estimated loss of 1 to 2 Kg of metal per matrix. Considering that the bath must be renewed when the sodium aluminate concentration reaches 200 Kg/m³ and that, in Europe, 1.55 million tons of aluminum were extruded in 1999, it can be calculated that around 12,000 m³ of this residue was produced. In the year 2001, this amount will increase to

Table 1. Experimental conditions of previous tests series, and the optimal ones for the zeolites studied in this paper.

Zeolite type	SiO ₂ /Al ₂ O ₃	Na ₂ O/Al ₂ O ₃	H ₂ O/Al ₂ O ₃	T (°C)	Exp. No.
4A	1.6-2.5	1.6-3.8	45-190	70- 80- 90	36
13X	2.9-4.3	2.9-6.0	85-200	80-90-100	24
Y	15-20	20-24	200-400	90-95-100	16
HZSM-5	20-30	1.0-3.0	600-1400	125	4

Optimal Conditions

Zeolite type	Chemical composition of the gels	Aging	T (°C)	t (h)
4A	2.70Na ₂ O:Al ₂ O ₃ :2.08SiO ₂ :109.78H ₂ O	No	80	3*
13X	4.21Na ₂ O:Al ₂ O ₃ :3.48SiO ₂ :168.43H ₂ O	Yes	80	6
Y	6.0Na ₂ O:Al ₂ O ₃ :18SiO ₂ :320H ₂ O	Yes	95	15
HZSM-5	28Na ₂ O:Al ₂ O ₃ :400SiO ₂ :12TPABr:1400H ₂ O	No	125	24*

* under agitation

approximately 14,000 m³. These wastes along with those coming from the above-mentioned pickling baths, create a very important waste disposal problem.

The synthesis of zeolites from industrial residues has been seriously considered in recent years. Various articles have appeared in the scientific literature, including ones describing fly ash using to produce zeolites 4A and 13X [3, 4], rice husk ash for ZSM-48 [5], used catalysts from the FCC refineries for 4A [6], and wastes from aluminum industry for 4A and 13X [7-9].

This paper presents results obtained in the synthesis of 4A, 13X, Y, and ZSM-5, using residual effluents from the aluminum industry. Due to the special characteristics of the raw materials, emphasis has been made on the study of the chemical impurities within the residues that may affect the properties of the synthesized products. These impurities come from the alloy to be anodized. Thus, for example, the chemical composition of Alcoa 6063, one of the most used, is the following: Al 98-99%, Si 0.3-0.6%, Fe 0.1-0.3%, Cu 0.1%, Mn 0.3%, Mg 0.4-0.6%, Cr 0.05%, Zn 0.15%, and Ti 0.2%. Other significant impurity sources are from recycling of previously anodized profiles that contaminate the pickling baths with foreign ions, such as Ni, Sn, and F.

ZEOLITE SYNTHESIS

The general synthesis procedure consisted of the preparation of gels with an adequate composition mixed in a stirrer at 1,500 rpm for 30 min and then crystallized at temperatures between 80 to 120° C. For zeolites 13X and Y, the gel was allowed to rest at ambient temperature for 24 hours. For zeolites 4A and HZSM-5, they were crystallized directly, stirring at 100 rpm [10]. The syntheses were carried out in polyethylene flasks, except in the case of HZSM-5, which was crystallized in a carbon steel autoclave. The crystalline solids were separated by filtration or centrifugation, washed with water until pH 8, and then dried at 120° C.

In previous papers [7, 9], we studied the influence of the reaction conditions, such as chemical composition of the reactive medium, temperature, and reaction times (aging and crystallization) on the reaction rate and on the crystallinity of the products. Table 1 summarizes these experimental results. The synthesis of zeolites 4A and 13X was optimized through experimental design, determining the optimal SiO₂/Al₂O₃, Na₂O/Al₂O₃, and H₂O/Al₂O₃ molar ratios that defined the batch composition [9, 11]. These values have been used for the synthesis of the samples studied in this paper (see Table 1). For the synthesis of zeolites Y and ZSM-5, the molar ratio values were selected from previous experiments.

As a source of aluminum, two types of alkaline residues were employed: a) from anodizing plant pickling bath, with a composition of 50 to 200 g/l of NaAlO₂ and 100 g/l of NaOH; and b) from extrusion matrix cleaning bath, with a composition of 200 to 300 g/l of NaAlO₂ and 100 to 250 g/l of NaOH. Prior to synthesis, the liquid effluents were centrifuged in order to eliminate impurities in suspension. The effluent from the pickling bath was used for the synthesis of zeolites 4A and 13X, while that from the matrix cleaning bath for zeolites Y and ZSM-5.

As silica sources: a) a reagent grade sodium silicate solution supplied by Industrias Químicas del Ebro (Spanish company), with a density of 1.360 g/ml and SiO₂/Na₂O ratio of 3.24, and b) precipitated silica Neosyl TS from Crosfield Ltd., with a specific surface area of 200 m²g⁻¹. Reagent grade sodium hydroxide and tetrapropylammonium bromide were also used.

CHARACTERIZATION METHODS

The solids were studied and characterized by X-ray diffraction, specific surface area, particle size distribution, scanning electron microscopy (SEM), whiteness, cation exchange capacity (CEC), and chemical composition.

The X-ray diffraction analysis was carried out using a Philips PW-1840 diffractometer, with Cu Kα radiation. The sample composition was estimated using flu-

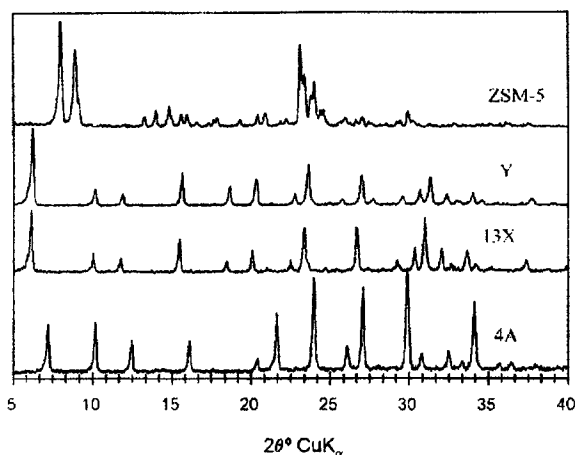


Figure 1. X-ray diffractograms of synthesized zeolites.

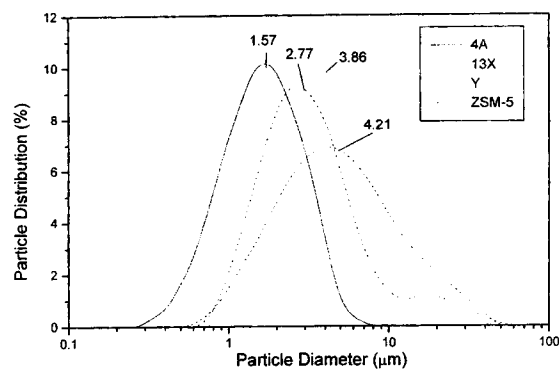


Figure 2. Distribution of particle size of the synthesized samples.

orite (CaF_2) as an internal standard (1:1 mixtures). The particle size distribution was measured by laser scattering of an aqueous dispersion of zeolite (solution of calgon as dispersant) using a Malvern Instruments Mastersizer S apparatus. Nitrogen adsorption-desorption isotherms were determined with a Micromeritics ASAP 2010 after degassing the samples at 110°C for 4 hrs to a residual pressure of 10^{-5} torr. Calculation of the BET surface area was performed using the equipment software. The whiteness was determined with a Minolta 2002 spectrophotometer, following the ASTM 313 standard.

The chemical composition of the residual effluents was determined in two ways: a) by titration of sodium aluminate with HCl followed by complexing the aluminum, precipitated as $\text{Al}(\text{OH})_3$ with potassium fluoride, and a second titration of released OH ions with HCl and, b) precipitating the effluent with HCl at pH 6.5, then filtering, washing, and calcining at 600°C , and finally analyzing the content of elements by X-ray fluorescence in a Philips model PW 1404 sequential spectrometer. The chemical composition of the zeolites was also determined by the latter technique.

In order to measure the CEC, the samples were dried at 350°C for 3 hrs. Then they were kept in stirred calcium or magnesium chloride solutions for 24 hrs at 20°C . After filtering, the solutions were titrated with EDTA, using murexide (for Ca^{2+}) and eriochrome black (for Mg^{2+}) as indicators.

RESULTS AND DISCUSSION

The X-ray patterns of the synthesized samples are shown in Figure 1. The sharpness of the peaks are indicative of the high crystallinity of the materials. Thus, using the profile width of peaks measured by XRD, we calculated crystallite sizes of 150 to 200 nm. No peaks corresponding to foreign phases were observed, indicating that the maximum content of impurities in these samples was below the detection limit of this technique (5%).

Figure 2 shows representative particle size distributions of the four zeolites. The 4A zeolite had the

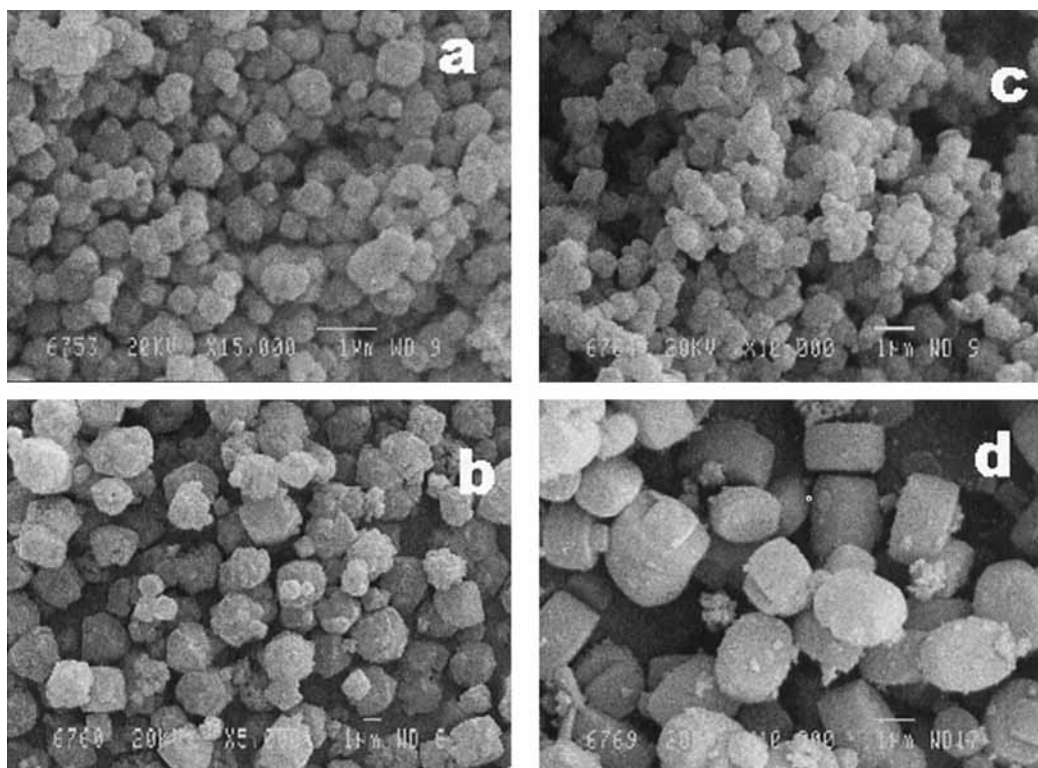
smallest average particle size, d_{50} , $1.57\ \mu\text{m}$. Samples of 13X, Y, and ZSM-5 samples had average sizes of 2.77, 3.86, and $4.21\ \mu\text{m}$, respectively.

The morphology of samples was investigated by SEM. Zeolite A forms euhedral crystals of cubic and rhombic dodecahedral shape, showing rounded corners, with sizes between $0.4\text{--}0.9\ \mu\text{m}$, that formed aggregates of $2\text{--}3\ \mu\text{m}$ with reticular structure (Figure 3a). For sample 13X, non aggregated cubic-octahedral, along with inter-growth crystals, with an average size between $2\text{--}2.5\ \mu\text{m}$ were observed (Figure 3b). These figures are compatible with a d_{50} value of $2.77\ \mu\text{m}$, which was obtained by laser. In the micrograph for the Y sample, small cubic-octahedral crystals of between $0.3\text{--}0.6\ \mu\text{m}$ were observed that form aggregates of $3\text{--}6\ \mu\text{m}$, compatible with the value of $3.86\ \mu\text{m}$ d_{50} (Figure 3c). For the HZSM-5 sample (Figure 3d), disc shapes were observed with the basal faces frequently twinned, giving rise to the typical morphology of this phase [12]. The average particle size was between $0.6\text{--}2\ \mu\text{m}$, similar to the previously published value [13]. Aggregates of reticular structure with sizes greater than $4\ \mu\text{m}$, compatible with the d_{50} of $4.21\ \mu\text{m}$, were also observed.

The BET surface areas measured for samples Y and ZSM-5 (the only synthesized samples with potential applications in catalysis) were 675 and $390\ \text{m}^2\text{g}^{-1}$. The values usually reported for zeolite Y lie between 600 to $900\ \text{m}^2\text{g}^{-1}$ and zeolite ZSM-5 lie between 300 to $400\ \text{m}^2\text{g}^{-1}$ [13, 14].

The CEC and whiteness were only measured for samples with low Si/Al ratio, since they are the ones with a possible detergent application. The CEC of 4A was $3.04\ \text{mmol/g}$ (measured with Ca^{2+}) and that of 13X, $2.98\ \text{mmol/g}$ (measured with Mg^{2+}). For the whiteness of samples 4A and 13X values of 96.56 and 97.51% , respectively, were obtained. This means that the products obtained fulfilled the requirements for the formulation of detergents.

The chemical compositions of the alkaline residues before and after centrifuging are presented in Table 2. It may be seen that changes on the concentrations of NaOH and NaAlO_2 were negligible. On the contrary,



Figures 3a, b, c, and d. SEM micrographs of: a) 4A zeolite, b) 13X zeolite, c) Y zeolite, and d) ZSM-5 zeolite.

some of the minority elements suffered remarkable changes in composition: Mg (completely eliminated), Ni, Co, Mn, Fe, Cu, and V (reduction between 50 and 90%). Others such as F, S, Ca, Cr, Zn, Cd, Sn, and Pb, did not change.

The chemical composition of the synthesized zeolites is presented in Table 2. The heavy metal content was relatively low, between 8 to 30 ppm, except for Fe, which was between 58 to 101 ppm. The content of Cd, Co, Mg, Mn, Pb, Sn, V, and Zn was lower than the analytical detection limit.

The relative variation of each element during the crystallization process may be determined by considering that all the aluminate of the effluent goes to form part of the zeolite (analyses indicate 99%). Thus, by establishing the E/Al ratio for each element the enrichment or depletion of minor elements, in the zeolites may be quantified. In Figure 4, these relationships are presented for the four effluents and for samples 4A, 13X, and Y. In this study, ZSM-5 could not be considered, due to the fact that, as the synthesis took place in an autoclave, the sample was contaminated with foreign heavy metal cations. As shown in both figures, the E/Al ratios were always lower in the zeolites than in the effluents, except in the case of F/Al for sample Y, which was slightly higher. The facility with which F can introduce itself into the zeolite framework justifies this anomaly [15].

Impurities content in the zeolites is very important. High heavy metal ion contents make the application of zeolites for detergents or catalysis impossible, because, on one hand, they promote the decomposition of perborate or percarbonate in detergents, provoking a

fall in their bleaching power [16], and, on the other hand, they can exert deleterious effects in catalysis [17].

From an ecological point of view, heavy metal cation concentrations in detergent zeolites are important since, after washing, zeolite degradation processes take place in the domestic sewage pipes, treatment plants, or surface waters. Depending on the chemical conditions of the aquatic system, the elimination of the aluminosilicates occurs via calcium aluminum phosphates or the formation of insoluble gibbsite/halloysite (in the absence of calcium/magnesium and phosphate). If heavy metal cations are present, they can be incorporated into the lattices of the corresponding minerals or similar amorphous precipitates [18]. When the content of these elements in the zeolites is lower, their adverse environmental impact is reduced. Therefore, the selection of the synthesis method and the control of the impurities are very important.

Two residues are produced by this synthesis method. The first is slurry from centrifuging the alkaline baths, composed of a mixture of heavy metal oxides, magnesium hydroxide, sulfates, and other impurities. This slurry is approximately 0.1% of the initial volume. The second residue is the mother liquor produced from the synthesis with high contents of sodium silicate and hydroxide, and small concentrations of Ca, K, SO_4 , and heavy metal cations. Part of these can be reused in new syntheses and the excess can be eliminated by neutralization and centrifugation.

We conclude that zeolite syntheses of waste streams from alkaline operations of the aluminum industry are possible. Employing the residues produced in Europe during the year 2001, around 20,000 tons of zeolite 4A

Table 2. Chemical composition of the alkaline effluents used in the syntheses and the products obtained.

	Raw Materials				Products			
	Pickling	Cleaning	Pickling Centrif.	Cleaning Centrif.	4A	13X	Y	ZMS-5
NaAlO ₂ (g/L)	122.6	259.2	122.6	251.7				
NaOH (g/L)	50.1	129.0	49.2	125.9				
SiO ₂ (% w/w)					32.92	37.87	48.45	98.70
Al ₂ O ₃ (% w/w)					27.93	23.83	17.35	1.17
Na ₂ O (% w/w)					16.98	14.54	10.55	0.70
H ₂ O (% w/w)					22.18	23.80	23.65	-
Density (Kg/L)	1.196	1.446	1.200	1.446				
Impurities (mg/g)								
F	0.607	0.295	0.439	0.163	0.606	0.542	0.565	0.150
Mg	0.196	0.571	-	-	-	-	-	-
S	1.146	0.031	1.088	0.031	0.125	0.030	0.038	0.032
K	0.031	0.094	0.018	0.080	0.062	0.054	0.068	0.056
Ca	0.024	0.014	0.025	0.012	0.082	0.063	0.010	0.050
Ti	0.004	0.010	0.002	0.008	0.008	0.008	0.008	0.008
V	0.002	0.032	0.002	0.006	-	-	-	-
Cr	0.003	0.057	0.001	-	0.008	-	-	0.020
Mn	0.008	0.029	0.002	0.005	-	-	-	-
Fe	0.085	0.147	0.014	0.101	0.082	0.058	0.073	0.092
Co	0.002	-	-	-	-	-	-	-
Ni	0.485	0.008	0.005	0.004	0.008	-	-	0.014
Cu	0.021	0.014	0.003	0.015	-	-	0.011	0.012
Zn	0.003	0.015	0.002	0.013	-	-	-	-
Cd	0.002	-	0.002	-	-	-	-	-
Sn	0.319	-	0.285	-	-	-	-	-
Pb	0.015	0.047	0.011	-	-	-	-	-

could have been produced. This was equivalent to 5% of the European production of this material [19]. The physico-chemical properties, like crystallinity, CEC, particle size, and whiteness, are perfectly adjusted to the requirements of the detergent industry.

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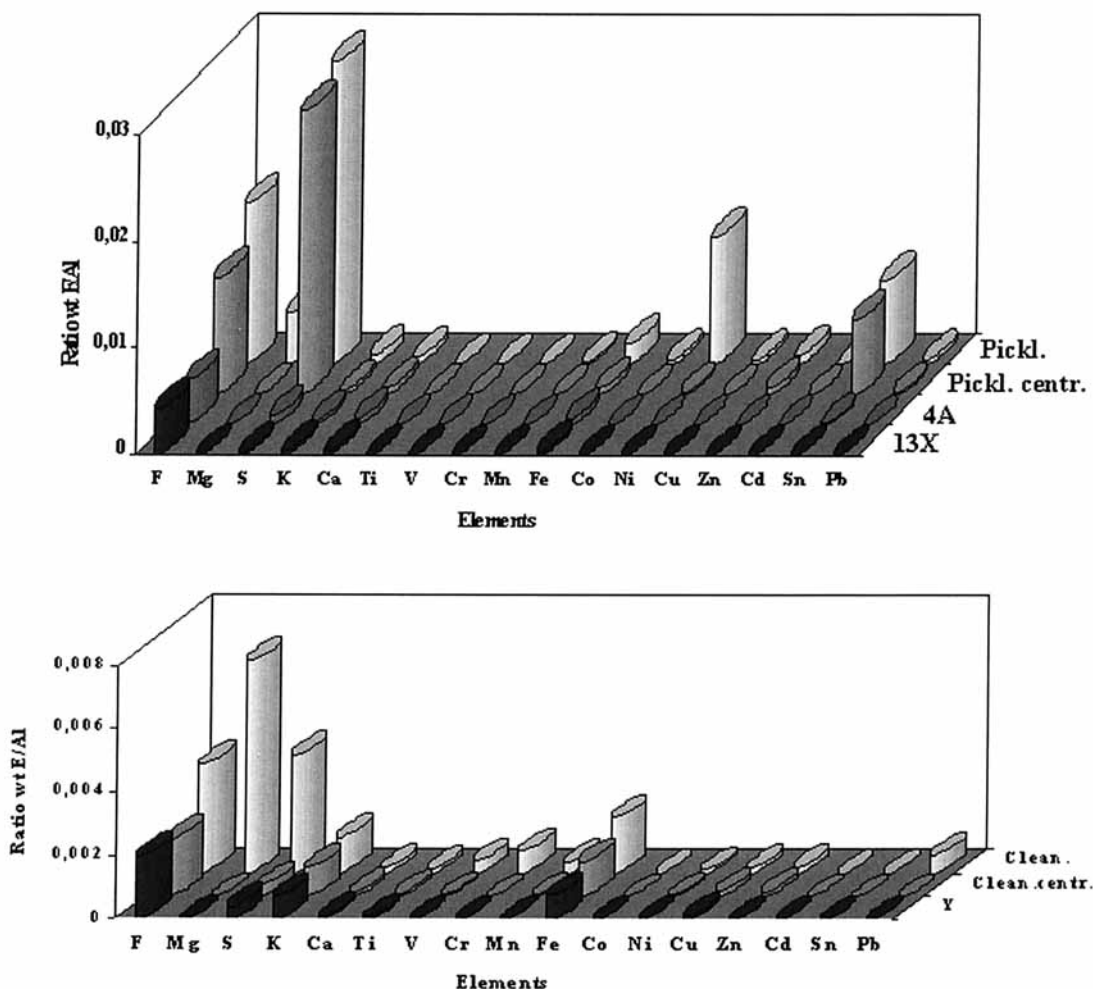


Figure 4. Relative variation of the impurities during the crystallization process.

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