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IDENTIFICATION OF THE CRYSTALLINE AND AMORPHOUS PHASES IN THE DRIED RAW ALUMINA HYDROXIDE

Gheorghe DOBRA[1], Viorel BADILITA[2], Sorin ILIEV[1], Lucian COTET[1], Laurentiu FILIPESCU[3*], Alina BOIANGIU[1]

The crystalline and amorphous phases, excepting the gibbsite, from the samples collected at temperatures 120-160ºC have a low crystalline degree or at least are intensely eroded (being phases transported as small particles by the heating gases of the moist hydrate). As a result, quantitative determination of these phases in the samples collected at temperatures 120-160ºC proved to be a difficult problem, even if, the measuring instrument is an advanced one and the Rietveld finishing program has been applied. The paper describes a method of identifying and characterizing these phases and provides information about this grade of alumina hydroxide availability and marketability.

Keywords: alumina hydroxide, mineralogy, phases, drying, identification

1. Introduction

Aluminum hydroxide as non-metallurgical alumina has many uses and the most important of them are: a) manufacture of the water and industrial water treatment agents; b) manufacture of aluminum fluoride and cryolite, and other chemicals, such as zeolites and pure and ultrapure sodium aluminate; c) manufacture of the flame retardant fillers and materials; d) manufacture of the special alumina, such as: activated alumina, tabular alumina, oxides for the production of tricalcium aluminate cements, polishing materials and oxides for the manufacture of molten alumina and mullite; e) oxides for the refractory materials, for the manufacture of ceramics and for the manufacture of frits and fritted materials; Another category of special alumina is used for the manufacture of high brightness pigments, inks, glass and glazes, especially for special paints and additives for epoxy materials. All the aluminum hydroxide (alumina hydrate) consumers are highly requiring products of good quality and, in this specific problem, the purity of alumina hydrates means both chemical and mineralogical purity. Actually, the customers are asking for $Al(OH)_3$ as gibbsite mineral phase.

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[1] SC ALUM SA, Tulcea , Romania, e-mail: dobra@alro.ro

[2] INCD IMNR Bucuresti, Romania, e-mail: viorelbadilita@yahoo.com

[3] * Corresponding author, Doctoral School of Chemical Engineering, University POLITEHNICA of Bucharest, Romania, e-mail: laurentiu_filipescu@yahoo.co.uk

The purpose of the investigation was to identify and quantitatively measure the concentration of all crystalline and amorphous phases present in the dry material obtained in the preliminary phase of heating (in cyclone 1, calcination plant for alumina production), as an effect of the advanced dehydration due to the local or accidental overheating of the moist hydrate in this production stage (reaction 1).

To highlight the effect of temperature on the formation of crystallographic phases other than the gibbsite, the temperature of the material in the preheating zone was reduced in several steps from 160ºC to 120ºC. The drop in the temperature was made by the admission of cold air in the heating gas coming from the last calcination step. Thus, samples were collected at 120, 130, 140, 150 and 160 ° C. The entire paper is intended for the complete characterization of dry hydrate as a salable product.

2. Experimental

2.1 Aluminum hydroxide samples

The samples were collected from cyclone 1 of the calcination plant (*Table 1*).

Table 1

Samples collected for analyses

No.	Sample name	Draying temperature, ºC	Collecting and procrssing
1	H105	105	From dried, milled and classified aluminium hydroxide, special products class
2	H120	120	From Cyclone 1 and milled
3	H130	130	From Cyclone 1 and milled
4	H140	140	From Cyclone 1 and milled
5	H150	150	From Cyclone 1 and milled
6	H160	160	From Cyclone 1 and milled

The first product H105 belong the new class of special dried aluminum hydroxide. This new grade of aluminum hydroxide was obtained and processed with the following equipment: Independent equipment / Installation for research and development of technology to obtain dried aluminum hydroxide", "Independent equipment / Installation for research and development of the technology of grinding and screening the dried aluminum hydroxide.", and "Independent equipment / Installation for research and development of the technology of wet aluminum hydroxide classification.", parts of the European project: "Endow the Research & Development Department of SC ALUM SA with independent and efficient research facilities to support the economic competitiveness and business development (Financing Contract nr.64/08.09.2016, ID: P_34_286, Cod SMIS: 103867.

The other samples were collected from the low temperature cyclone 1 in the calcinations plant at Alum SA Tulcea (the applied old technology). The moist hydrate, before being collected as sample, has been standing in contact with the hot re-circulated gases from the calcination furnace a very short time, but enough to reach a temperature of about 160ºC, and to dry completely. Above this temperature it might lose some of its hydration water.

$$Al_2O_3.3H_2O=2AlO(OH)=2H_2O \quad (1)$$

Theoretically, temperature and time retention are insufficient to produce significant crystallographic changes due to the de-hydroxylation reactions, which basically start with significant speed above 290°C. However, other crystalline or amorphous phases, another than gibbsite, have been frequently reported in the dry material.

2.2. Sample processing

The analysis of the crystalline and amorphous phases in the collected samples was done by the X-ray diffraction method. A Bruker diffraction unit and a Rietveld refining program were used for this purpose. X-ray analysis was correlated with a standard simple method of evaluating the quality of dry hydrate. The latter method consists in dissolving a quantity of 20 g of Al_2O_3 as (Al_2O_3 • $3H_2O$) in 100 g 32% HCl, followed by measuring the mass of the non-dissolved fraction. If the non-dissolved mass is less than 2 g, the product is accepted as dry non-metallurgical hydrate. Since the identification of all crystallographic phases could be performed qualitatively, but the quantitative measurement of the concentrations of these phases in the collected samples could not be carried out precisely (due to their low crystallinity of the qualitatively identified phases). More additional X-ray diffraction analyses were required for the residues remaining after dissolution of the samples in 32% HCl, in order to know the concentration of each individual mineralogical phase accumulating in the analyzed residue

2.3. Sample preparation for X-ray diffraction

A sample of 4.0000 g of each sample subjected to DRPX analysis was mixed with 1.0000 g ZnO from Johnson Matthey, Materials Technology, UK. Zinc oxide serves as an external standard for quantitative phase analysis (it is not found in any of the initial samples). This mixture was ground for homogenization and micronized up to particle sizes of the order of ~1 μm. For the purpose of mineralogical phase analysis by the DRXP method, part of the sample obtained previously was loaded frontally into a 1mm deep quartz mono-crystalline support, with a diameter of 30mm. The surface exposed to radiation was leveled and flattened. In this way we obtained six samples from fresh dried aluminum hydroxides, containing all of its mineralogical phases.

Similarly, a second sample of approximate 20 ÷ 25 g from the material under analysis was solubilized in concentrated HCl, in order to clear up by DRXP, the nature of the HCl insoluble crystalline phases in each type of hydrate received for analysis. The residue from the dissolution in HCl was dried and manually milled in agate mortar for homogenization and micronization. Part of it was loaded frontally into the quartz carrier described above. The surface exposed to radiation was leveled and flattened. In this way we obtained another six samples coming from residues of the hydrate dissolution in HCl.

2.4 Equipment

Data acquisition was performed on the BRUKER D8 ADVANCE diffractometer using the DIFFRACplus XRD Commender software (Bruker AXS) and the Bragg-Brentano diffraction method, coupling Θ - Θ in vertical configuration.

Data processing was done using the DIFFRACplus BASIC Evaluation Package, version EVA12, 2006 from the DIFFRACplus BASIC (Bruker AXS) software package.

The identification of the compounds (qualitative phase analysis by DRXP) was performed using the software EVA12 - Search / Match Module [1] and the database provided by ICDD PDF-2 Release 2006 [2]. Quantitative phase analysis was performed using the Rietveld method and the DIFFRACplus TOPAS Version 3.0 software (Bruker AXS) [3], [4]. Structural data required by quantitative analysis Rietveld have been retrieved from the data bases: Crystallography Open Database [5] şi The American Mineralogist Crystal Structure Database [6], for all the identified crystalline compounds. To determine the content of amorphous material, the external standard method, described by O'Connor & Raven [7] and Madsen & Scarlett [8] was used. A known amount (20%) of ZnO - zincite was added to each sample. In this approach, each identified crystalline phase is quantified relative to the external zincite standard.

The content of amorphous material is given by the difference between 100% and the sum of the concentrations of all identified and quantified crystalline phases. Content of amorphous material in each sample, thus determined, generally represents the solid amorphous phases, the liquid phases retained in the porosity of the material (moisture, salt solutions, etc.), poorly crystallized and / or undetected phases, all them of being at low concentrations. We mention that this approach has been successfully used and validated in several X-ray diffraction studies, performed to identify and quantify the products obtained during the thermal decomposition of aluminum hydrates [9]. The Figs. 1-4 are illustrating our data processing. Regarding the residues from the dissolution in HCl, the quantitative phase analysis was performed by the Rietveld method assuming that all phases are crystalline and are identified. In this approach, the sum of the mass concentrations of all the quantified crystallized phases is 100%. In this context, the content of amorphous material (which generally refers to the weakly crystallized and / or undetected phases and / or liquids retained in the porosity of the studied powder) was ignored, being considered negligible.

3. Results and discussion

3.1 Dissolution in 32%HCl

The results of analyzes carried out are presented in *Table 2* and in the Fig. 1-4. According to these analyzes, it results that the dissolution in 32% HCl, as the standard method of evaluation the quality of aluminum hydroxide, leads in this case to expected results i.e. the mass of residue is less than 2 g, which is the accepted threshold.

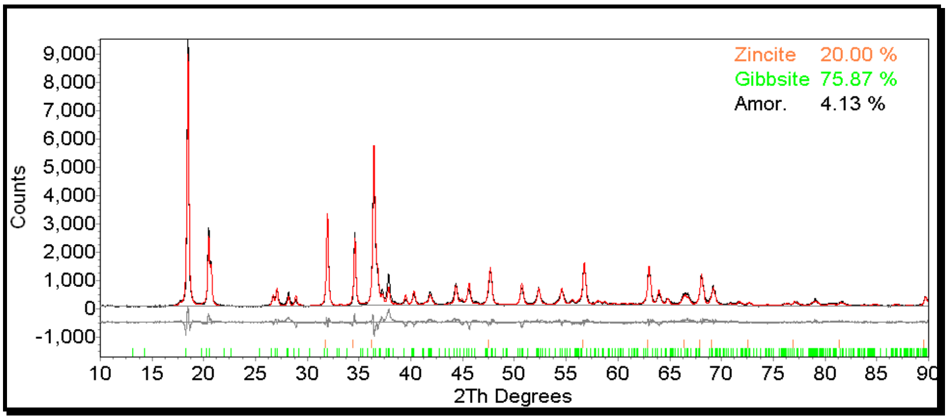

Fig. 1. Aluminium hydroxide dried at 105°C. Rietveld quantitative DRPX analysis. $Al(OH)_3/ZnO$ (80/20 mass)

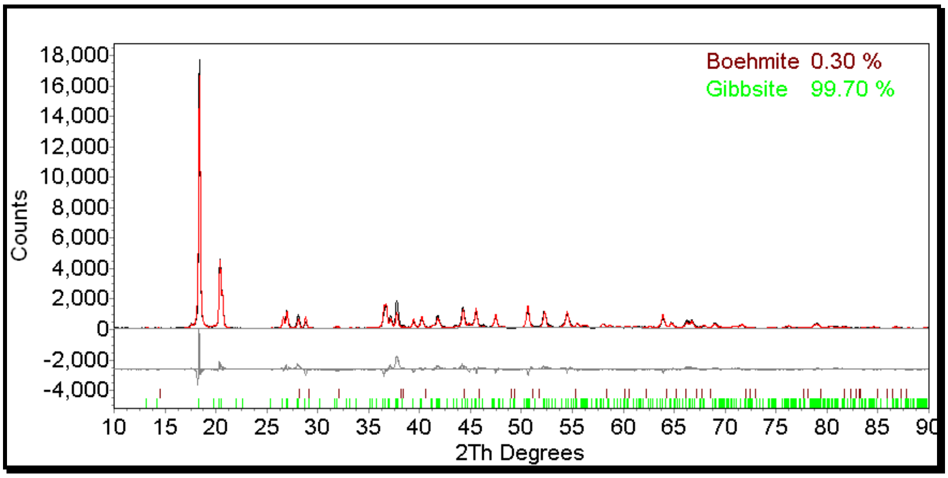

Fig. 2. Aluminium hydroxide dried at 105°C. Rietveld quantitative DRPX analysis HCl 32% dissolution residue

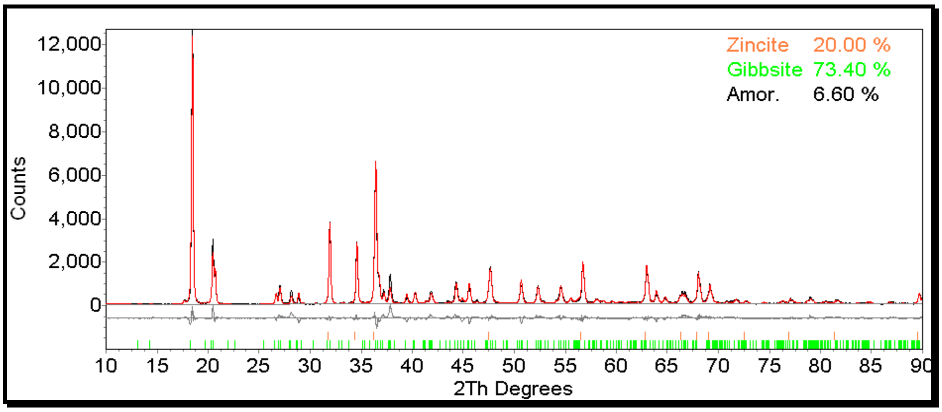

Fig. 3. Aluminium hydroxide dried at 160ºC. Rietveld quantitative DRPX analysis. $Al(OH)_3/ZnO$ (80/20 mass)

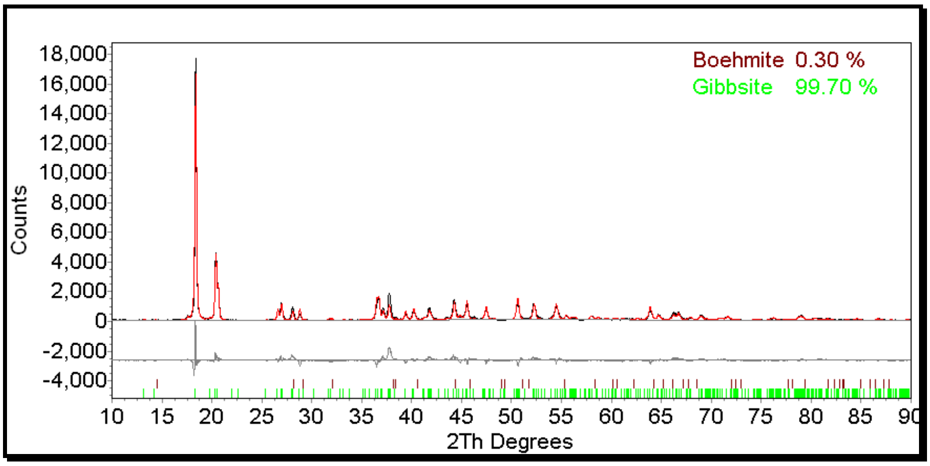

Fig. 4. Aluminium hydroxide dried at 160ºC. Rietveld quantitative DRPX analysis. HCl 32% dissolution residue

Table 2

Mass of the residue left after the dissolution of samples in 32% HCl, according to the standard method

Crystaline phase	Samples					
	H105	H120, %	H130, %	H140, %	H150, %	H160, %
Residue mass, g	0	1.4216	1.868	1.9991	1.7453	1.8095
Dissolved mass fraction, %	Full dissolution	7.11	9.03	9.59	8.72	9.05

From Fig. 5 it can be seen that non-dissolved fraction is smaller in the case of the sample collected at 120ºC. The non-dissolved fractions of the other samples are distinctly different from the one at 120ºC, but they vary quite little between 130 and 160ºC. It is possible that the difference between the non-dissolved fractions in the samples collected between 130 and 160ºC and the non-dissolved fraction in the sample collected at 120ºC comes from the dust generated by the hot gases used to dehydrate the moist hydrate.

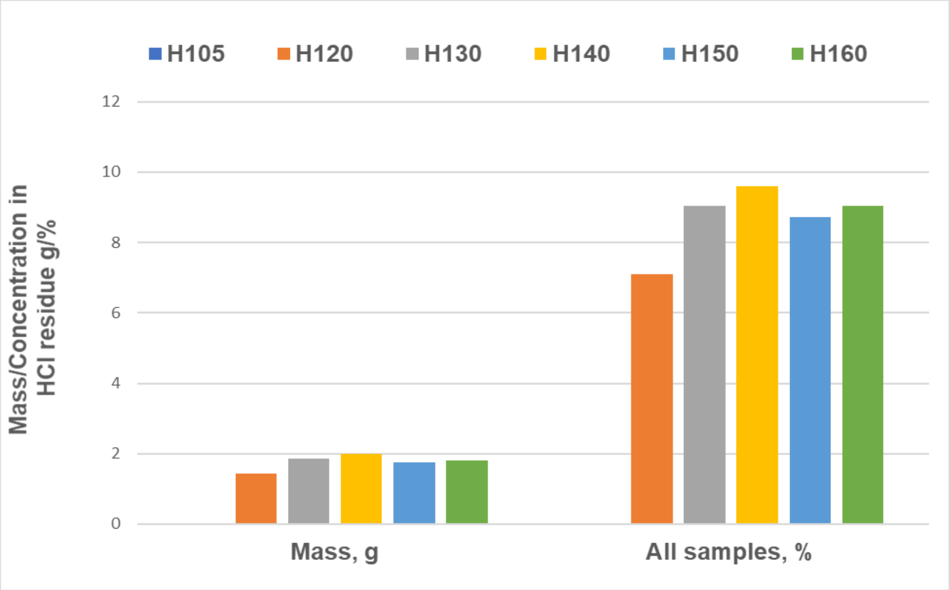

Fig. 5. Residues mass after dissolution and the non-dissolved phases concentration

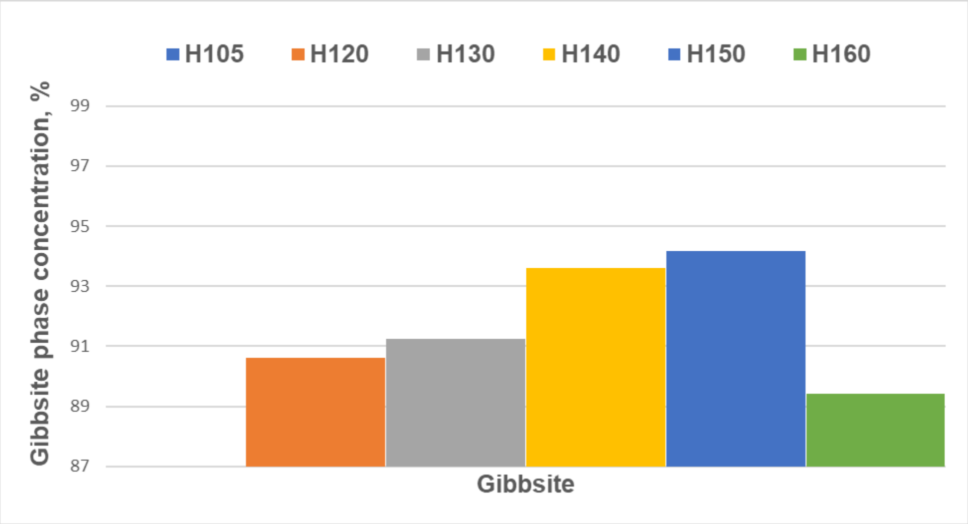

Fig. 6. Content of the gibbsite, as mineralogical phase, in the non-dissoloved residues

If this hypothesis is valid, then alpha and gamma phases should be identified in these samples. As it can be seen from the *Table 3*, and Fig. 6 and 7, the above hypothesis is verified.

For example, from the Fig. 6 it is easy to see, that most of the gibbsite was dissolved in hydrochloric acid (the smallest fraction of gibbsite in the residue) in the case of sample collected at 120ºC**.,** excepting the sample H105, which is pure gibbsite phase.

Table 3

Gibbsite content in the residue samples from at the temperature: 120ºC, 130ºC, 140ºC, 150ºC and 160ºC

Crystaline phase	Samples					
	H105	H120, %	H130, %	H140, %	H150, %	H160, %
Gibbsite	99.9	96.0	91.3	93.5	-	91.7

Table 4 and Fig. 7 show that the gamma phase is present at the highest concentration in the sample collected at 120ºC.

The alpha phase predominates in the sample collected at 140 °C, and the boehmite phase predominates in the sample collected at 160 °C.

The fact that the gamma and alpha phases occur at low temperatures in a large proportion, but without significant differences from the other samples, is a proof that these phases come from the moist hydrate heating gases.

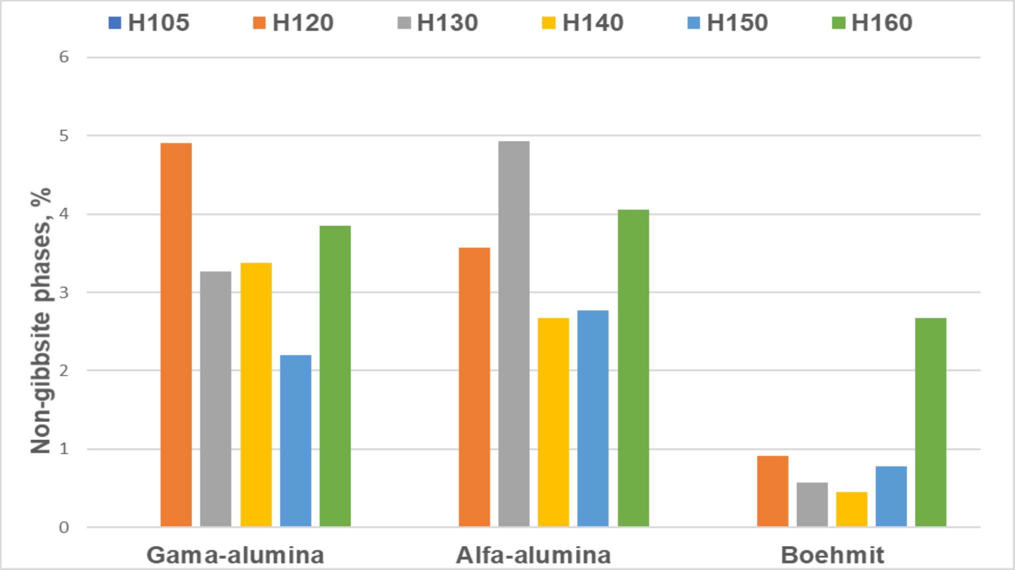

Fig. 7. Non-Gibbsite phases in the HCl dissolution residue samples**.**

Table 4

Phases composition of the residues solubilized in HCl 32%

Crystaline phase	Samples					
	H105	H120, %	H130, %	H140, %	H150, %	H160, %
Gibbsit	-	90.6	91.23	93.59	94.16	89.43
Gama-alumina	-	4.9	3.27	3.38	2.29	3.85
Alfa-alumina	-	3.57	4.93	2.57	2.77	4.05
Boehmite	-	0.91	0.57	0.45	0.78(22)	2.67

Table 5

Phases compositon in the residue

Crystaline phase	Samples					
	H105, % (1)	H120, % (2)	H130, % (3)	H140, % (4)	H150,% (5)	H160,% (6)
Gibbsit	100	96.0	91.3	93.5	93.0	91.7
Other phases	. 0	4.0	8.7	6.5	7.0	8.3

The fact, that in the sample collected at 160ºC, the bohemite content is 3-4 times higher than the boehmite content in the samples collected at the other temperatures, shows that at temperature of the 160ºC, dehydration of the dry hydrate begins and that the mechanism followed by the dehydration of the gibbsite is gibbsite → boehmite → higher temperature range phases, also mentioned in the literature as valid for small particles and higher heating speeds [9, 10]. As a result, the hydrate extracted from cyclone 1 at 160 ° C is not a marketable product as dry hydrate.

3.2 Analysis of samples collected at temperatures 120-160ºC.

The crystalline and amorphous phases, excepting the gibbsite, from the samples collected at temperatures of 120-160ºC have a low crystallinity degree or at least they are strongly eroded (being transported in the form of small particles by the heating gases of the moist hydrate).

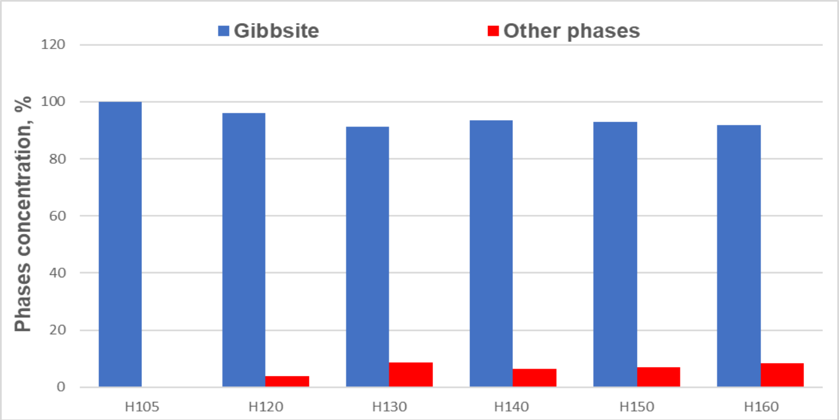

Fig. 8. Gibbsite and other phases in the residue samples

As a result, the quantitative determination of these phases in the samples collected at temperatures 120-160ºC proved to be a difficult problem, even if the measuring equipment is an advanced one, and the Rietveld finishing program has been applied.

The greatest difficulty was the evaluation of the amorphous phase concentrations. However, the concentration of the gibbsite, and the total concentrations of the other phases, including the amorphous phase, was accurately determined.

The data are presented in the table 5 and the Fig. 8. The biggest error is that the "amorphous" water also enters in the wastewater, which explains the content of 5% from total other phases than the gibbsite in the dry control sample 4-5 hours at 105ºC. Not the same thing is true for samples collected at 140-160ºC, where the wastewater is much less than 1% and the total of phases other than gibbsite in these samples is accurate and describes the real phase composition of these samples.

4. Conclusions

The results clarified some new sides of the gibbsite dehydration process at limits of the de-hydroxylation temperature and explained the nature of mineralogical phases at the transition point gibbsite ↔ boehmite.

The significant collection of the dry hydrate, from the low temperature cyclone 1 of the fluidized bed calciner in an alumina plant, at a temperature below 140ºC leads to a product that can be used for non-metallurgical applications, according to the hydrochloric acid dissolution test.

However, the application of this technology for obtaining dry hydrate remains dependent on purity of the re-circulated gases during the preliminary drying of hydrate in the early stages of fluidized bed calcinations of hydrate up to the gama alumina.The marketing of this product should be only temporary, until the construction of a drying, grinding and grading installation, in order to increase the quality of the product and to expand its fields of application.

Concerning behavior of the sample H105 and concluding that this sample is a pure gibbsite phase, it is rational to think that the new independent equipments purchased by SC ALUM SA Tulcea upon completion of the European project: “Endow the Research & Development Department of SC ALUM SA with independent and efficient research facilities to support the economic competitiveness and business development (Financing Contract nr.64/08.09.2016, ID: P_34_286, Cod SMIS: 103867, and recently put into operation, can produce new grades of aluminum hydroxide. Also, the capability of entire unit can be extended over delivery of fine grades of aluminum hydroxide as the raw materials for advanced technologies. Thus, for the first step, SC ALUM SA, can approach fumes and flame retardants and polymer stabilization technologies [11-14]. Then, SC Alum SA could enter among the suppliers of aluminum hydroxide for the medicines and cosmetics industry, respectively for the textile and inks, catalysts industry [15]. And finally, to find a path to ceramic and castable ceramic [16,17] and to tire tread rubber composite and other fine products [18].

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