THE POSSIBILITY FOR COMPLETE WASTE WATER PURIFICATION

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Abstract

It is known that the waste water from the factories for the nitrocellulose production contains sulphuric acid which is usually neutralized with lime giving the nitrogypsum ($CaSO_4 \cdot 2H_2O$) as the by-product. On that manner the problem of this waste water is only partialy solved because the nitrogypsum is dumped near the factory and exist as ecological problem.
In this paper the method for nitrogypsum dehydration with the purpose of useful product-hemihydrate of calcium sulphate ($CaSO_4 \cdot 0.5H_2O$) obtaining, was applied. This method is consisting of suspending the gypsum in aqueous solution of sulphuric acid with the different gypsum/acid solution mixing ratios, under p_{at}.After predetermined time the phases were separated by vacuum filtration, and the products were washed with boiled water, dried and investigated with DT, IR and microscopic analysis.
Obtained results indicates α-hemihydrate of calcium sulphate ($CaSO_4 \cdot 0.5H_2O$) formation for all suspensions of gypsum in acid solution (20 % mass.) with the slurry density below 0.6 g/cm^3. For the suspension with the higher slurry density dehydration reaction did not go to completion. It means that by the usage of this method the problem of the reutilization of obtained by-product and also of the waste water, can be finally solved.

Keywords: Nitrrogypsum; Alpha Hemihydrate; Slurry Density

Introduction

The mineral gypsum ($CaSO_4 \cdot 2H_2O$) has been formed for millions of years in the nature as a result of water evaporation from salt waters. It most frequently occurs in the grain form (mineral alabaster) and the fiber like form (mineral selenite). This mineral has for a very long period been used in the building industry to obtain gypsum binder (alpha and beta hemihydrate, and beta anhydrite), as cement additives for gypsum walls and panels, and as a substance for the solidification and stabilisation of different wastes, etc.

In addition to mineral gypsum, in the last decades, waste gypsum has appeared all around the world, the main origins of which are: the production of different acids (phosphogypsum, citrogypsum, borogypsum, tartargypsum and fluorogypsum), flue gas desulphurisation (FGD-gypsum), titanium oxide production, neutralisation of waste water containing SO_4^{2-} ions, etc [1-8].

The fact that gypsum is a sparingly soluble substance is a reason why waste gypsum dumps can be a significant source of sulphate ions in natural water and soil. Hence unprotected gypsum dumps represent an important ecological risk factor and thus waste gypsum recycling is very significant today. For this reason in the last years, there has been a growing interest for its application in the building industry and waste solidification/stabilization. There is particularly interest in the development of new cementitous binders, which would enhance the optimal utilization of several wastes: gypsum, fly ash, bottom ash (Fal-G binders) [6,7].

The sources of mineral gypsum in Serbia are limited and of very poor quality. For this reason, mineral gypsum is imported from neighbouring countries. On the other hand, our industry yields waste gypsums: phosphogypsum, citrogypsum and nitrogypsum. Also, in the near future, when the process of flue gas desulphurisation from thermopower and the other power plants commences, so-called FGD-gypsum will become available.

In previous studies, the possibility of the usage of two waste gypsums: citro-and FGD-gypsum for the production of the alpha hemihydrate of calcium sulphate was investigated [2,3]. For this purpose, a modification of the most modern and economic hydrothermal method, which consisted of suspending gypsum in unheated 20% mass aqueous solution of sulphuric acid under atmospheric pressure, p_{at}, was employed. The mechanism of calcium sulphate alpha-hemihydrate obtaining by this method has not yet been well investigated. Some autors states that the reaction evolves in the solid phase (solid-state mechanism). The other autors states that the reaction evolves in the solution (through-solution mechanism of reaction). There are also the opinion that the reaction simultaneously operates in the both these phases [3,4,8].

In this study, with the same aim, the gypsum, the waste obtained from the factory "Milan Blagojevic"-Lucani, which produces nitrocellulose was employed. The choice of a solution of sulphuric acid as the liquid medium for suspending and dehydration of gypsum is advantageous because of the potential possibility for the direct usage of part of the waste water (before neutralization) as the liquid medium. On that procedure the problem of waste water purification would be complete solved. This will be the subject of forthcoming investigations.

Experimental

The waste gypsum was subjected to classical chemical, qualitative IR (Perkin Elmer 782 instrument) and microscopic (American-Optical Stereoscopic Microscope) analysis.

The experiments were performed in a charge reactor with perfect mixing (n=600 r.p.m.) employing the following procedure: different quantities of waste gypsum were suspended in the same volume of 20 mass% sulphuric acid, for a predetermined period under p_{at}. In this manner, gypsum/acid solution suspensions with slurry densities of 0.05, 0.125, 0.25, 0.50, 0.60 and 0.75 g/cm^3 were prepared.

The products were separated by vacuum filtration, washed with boiling water in order to remove sulphate ions and dried at 105^0C. Subsequently, the obtained products were investigated by qualitative IR spectroscopy, as well as microscopic and DT analysis. The contact time of the phases was successively prolonged by five minutes until the hemihydrate was formed. In that manner, the time of gypsum dehydration, t_d, was determined. By dividing the waste gypsum mass with the time of dehydration, the rate of dehydration was calculated.

Hemihydrate formation was established by qualitative IR analysis using the method reported previously [2,3,8].

In the experiments where hemihydrate was not formed quantitatively, the contact of the phases was prolonged to three hours.

Results and discussion

The results of classical chemical analysis of the waste gypsum are presented in Table 1, from which it can be seen the relation CaO/SO_3 (0.78) is significantly higher than the theoretical value for gypsum (0.70). This fact, as well as the MgO content, indicates the presence of carbonate [7]. The qualitative IR analysis(Fig.1) confirmed the presence of carbonate (absorption band at 1380 cm^{-1}), which also showed the presence of nitrates (absorption band at 1440^{-1}) [11]. The presence of carbonate was the second reason for the selection of an aqueous solution of sulphuric acid as the liquid medium for gypsum suspension as it was assumed that the carbonates would be dissolved in the acid solution.

Table 1.Chemical composition of the employed nitrogypsum

Component	% mass.
CaO	23.77
SO_3	30.40
CaO/SO_3*	0.78
SiO_2 insoluble substances	1.03
Al_2O_3	-
Fe_2O_3	-
MgO	0.57
NO_3^-	0.99
CO_2	0.11
Loss of ignition	-
Crystal water	14.10
moisture	27.91
Organic substance	0.11

*Theoretical value of the CaO/SO_3 ratio is 0.7

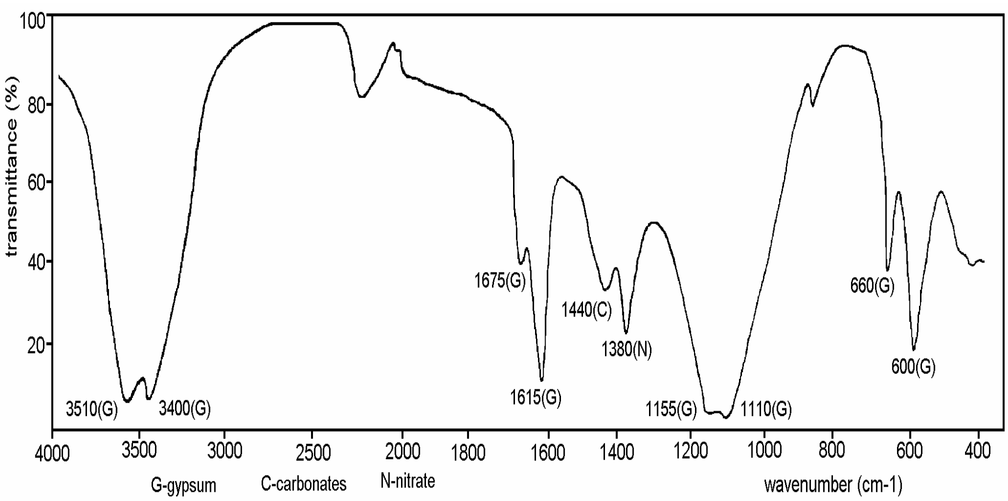

Fig 1. IR spectra of nitrogypsum

The microscopic analysis of the waste gypsum showed that it consisted of microcrystals and irregularly-shaped aggregates of the microcrystals with a very narrow range of size and an average length of the particles of 0.12 mm. This means that prior grinding and sieving was not necessity.

The results of the experiments are presented in Table 2. They show that the gypsum/acid solution mixing ratio (suspension slurry density) influenced the characteristics of the product and the rate of the gypsum dehydration reaction. The hemihydrate of calcium sulphate was formed in all experiments, with the exception for the experiment N^{o}6 with the highest slurry density, when the gypsum dehydration reaction did not go to completion. It is also evident that the rate of gypsum dehydration increases with increasing density of the suspension slurry.

Table 2. Influence of slurry density of nitrogypsum-acid solution suspension on the characteristics of the formed hemihydrate

Exp. No.	Slurry density	Product comp-osition	Rate of H.H. forma-tion	H.H. form	H.H.single crystal average length	Endotherm peak	First exotherm peak	Second exotherm peak
	g/cm^3		(g/min)		(μ m)	(^{0}C)	(^{0}C)	(^{0}C)
1	0.05	H.H.	0.1	α+β	18	167	216	354
2	0.125	H.H.	0.8	α	23	173	218	-
3	0.25	H.H.	1.2	α	28	178	220	-
4	0.50	H.H.	2.1	α	30	181	223	-
5	0.60	H.H.	2.8	α	38	184	225	-
6	0.70	H.H.+D.H.	-	-	-	-	-	-

H.H. - hemihydrate; D.H. - dihydrate

The microscopic observations of the obtained hemihydrates showed that in all experiments, with the exception of experiment N^{o}1, they consisted of transparent, translucent, compact, smooth, needle-like single crystals, the average lengths of which increased with increasing density of the suspension slurry. According to literature data, these observations indicate the high quality, alpha form of hemihydrate, which possesses good utilitarian properties, was obtained [4]. In the suspension with the lowest slurry density (experiment N^{o}1), in addition to hemihydrate with the cited characteristics, 11 vol % of porous, soft, white aggregates of microcrystals were formed. This hemihydrate form, according to literature data, corresponds to an inferior form of hemihydrate, the so-called beta hemihydrate [4]. The different qualities of these forms of hemihydrates result from the different surface areas of their particles and, consequently, of the different amounts of adsorbed water. Hence, the mechanical properties of the obtained dihydrate are different. The smooth and compact particles of alpha hemihydrate require a smaller quantity of water and give dihydrate with better mechanical properties than does the beta form of hemihydrate.

The results of microscopic analysis were confirmed by DT analysis. The DTA curves for the hemihydrate obtained in experiments 2, 3, 4 and 5 are typical for the alpha form, where one small exotherm directly follows a large endotherm [1,2,13]. The hemihydrate obtained in experiment N^{o}1 gave a different DTA curve, i.e., the large endotherm is followed with two small exotherms. The first exotherm directly follows the endotherm (characteristics for the alpha form) and the second, at a higher temperature, indicates the presence and the beta form of hemihydrate. The temperatures of these peaks on the DTA curves are also given in Table 2. The presented data show that with increasing density of the suspension slurry, the temperature of the endothermic peaks (167-181^{o}C) on the DTA curves increases, indicating a higher uniformity of crystal lattice of the obtained hemihydrates.

According to literature data, the temperature of the endothermic peaks for hemihydrate obtained from natural gypsum mineral are higher (>200^{o}C). Nature is better artist in crystal preparation than the laboratory [4,13]

In previous studies, [2,3] using the same method and identical experimental conditions, the alpha form was obtained from citrogypsum and a mixture of the alpha and beta form of hemihydrate from FGD-gypsum. These results can be explained by the different average particle size of the waste gypsum. From the waste gypsum with the largest average particle diameter (d = 0.2 mm), citrogypsum, only the alpha form of hemihydrate was obtained. This means that in this case the velocity of dihydrate dissolution exceeds the velocity of water molecule diffusion through the interior of the gypsum particles, i.e., only the “through-solution” reaction mechanism was operative. In the FGD-gypsum, the waste gypsum with the finest particle diameter, (d = 0.074 mm), these velocities are comparable and the both hemihydrate forms were obtained, i.e., the dehydration reaction occurs in the solid phase and in the solution. Waste gypsum with the middle particle diameter (d = 0.12 mm) gave the alpha form with one exception. The exception was the suspension with the lowest slurry density, from which both forms of hemihydrate were obtained, in this case, the rates of the gypsum dehydration reaction were significantly lower in comparison with the experiments 2, 3, 4 and 5, where only the alpha form was formed.

It is important to emphasise that the alpha form of hemihydrate obtained from the citrogypsum was a mixture of a two different phases: a phase of smooth single crystals of hemihydrate (average lengths 25-32 μm) and a phase of typomorphic aggregates (average lengths 60-82 μm), which according the literature data possesses inferior utilisation properties. Also the temperatures of the endothermic peaks of the DTA curves for the hemihydrates obtained from nitrogypsum were higher (167-181^oC) than those of the DTA curves of hemihydrate obtained from citrogypsum (164-169^oC).

Conclusion

The experimental results allow the following conclusions to be made:

- Dehydration of waste gypsum and hemihydrate formation is possible by suspending it in an unheated 20 mass % aqueous solution of sulphuric acid, under p_{at}, for slurry densities between 0.05-0.6 g/cm^3.
- With a gypsum/acid solution slurry density of 0.75 g/cm^3, the dehydration reaction does not go to completion, i.e., the product consisted of a mixture of hemihydrate and dihydrate.
- The obtained hemihydrates were nitrate free. In addition to having a high CaO/SO_3 value, they were also carbonate-free, which is important as the presence of carbonate is very detrimental for their usability.
- Whereas the dehydration of citrogypsum, the investigated waste with the largest average particle diameter, gave an alpha form composed of single crystals and typomorphic aggregates, which according to the literature possesses inferior utilisation properties, and the FGD-gypsum, the waste with the finest average particle diameter, gave a mixture of alpha (composed of needle-like single crystals) and beta forms of hemihydrates, the nitrogypsum, the waste gypsum with intermediate-sized particles, gave the alpha form of hemihydrate, composed of needle-like, single crystals. This form of alpha hemihydrate promises good usability. The exception being the suspension with the lowest slurry density (0.05 g/cm^3), where a mixture of both forms of hemihydrates was obtained.
- The rate of the waste gypsum dehydration reaction and the average lengths of the single crystals of hemihydrate, as well as their crystalinity, increased with the density of the suspension slurry, promising their better quality.

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