ALPHA PLASTER PRODUCED BY PRESSURELESS METHOD OF DEHYDRATION IN SALT SOLUTION

MARCELA FRIDRICHOVÁ, #KAREL DVOŘÁK, DOMINIK GAZDIČ

Brno University of Technology, Faculty of Civil Engineering,
Institute of Technology of Building Materials and Components,
Veveří 95, 602 00 Brno, Czech Republic

#E-mail: dvorak.k@fce.vutbr.cz

Submitted January 27, 2013; accepted December 11, 2013

Keywords: Alpha gypsum, Pressure less method, Salt solution

This study deals with development of production procedure of alpha plaster by the method of dehydration in salt solution, which is focused on the use chloride dusts as dehydration agent. For the dehydration of gypsum testing solution containing NaCl and KCl were used. Potassium chloride alone is unusable for dehydration, because simultaneously with the dehydration process the competitive process of gorgeyite creation occurs at a much higher reaction velocity. Sodium ions decrease the reaction velocity of goregyite formation. The mass concentration of 20 % dehydration solution containing 75 % of potassium chloride and 25 % of sodium chloride is optimal for mixed dehydration solution.

INTRODUCTION

The development of the manufacturing method initially faced the problem of poor availability of literary documents, both on technical and theoretical level. Efficiency of used salts is explained by the fact that they allow for faster transfer of heat, thus the dehydration may take place under lower temperatures (105 - 115°C). The water then escapes in liquid phase, which allows for emergence of alpha-hemihydrate.

In the world the principle of alpha-hemihydrate production by pressureless method in salt solution is used to a limited extent. Almost exclusively this concerns the preparation of hemihydrate in the solution of pure $CaCl_2$. This method is used for production of particularly hard plasters for dentistry. It is not used in construction industry, though it could represent a positive contribution in this industrial sector too. It allows obtaining high-quality a-plaster without the need for hydrothermal processing of gypsum [3, 5, 6, 7] and on quite technically undemanding equipment. Due to the need of high concentration of pure chloride salt solutions the economic demand of this method however would be the same, if not higher, than the traditional production in an autoclave. For this reason, it is essential to focus on the possibility of replacement of chemically pure salt by economically more efficient chloride salt obtained from secondary raw materials .

By selecting from among potential sources of chloride salt waste, a proposal was given to test cement dusts. These contain a high share of KCl, which may be extracted into aqueous solution. Through the initial performed study however it was discovered that pure potassium chloride is not suitable for dehydration purposes, because instead of dehydrating gypsum to hemihydrate it leads to emergence of the mineral gorgeyite, $K_2SO_4.5CaSO_4.H_2O$. However a minor addition of sodium chloride is able to reverse this undesirable process [1].

The present study is therefore aimed at finding the most suitable ratio of sodium chloride to potassium chloride to form mixed dehydrating solution and at finding the influence of its concentration of the resulting product morphology. Subsequently is proposed mechanism of the process.

EXPERIMENTAL

The basis of dehydrating solution was always chemically pure sodium chloride, to which potassium chloride was proposed as the second component. Due to the time required for the experiments was used instead of potassium chloride extracted from the flue dust qualitatively identical chemically pure KCl. Based on previous experience, the concentration of tested mixed solutions was set to the initial value of the 35 % mass.

List of composition of mixed dehydration solutions is presented in Table 1.

After finding the most suitable mixing ratio between NaCl and KCl was tested the optimal concentration of this mixed solution (the range 15 - 30 % mass) to achieve the best morphology of the resulting alpha plaster. The dehydrating process was always realized on laboratory dehydrating apparatus. This apparatus was developed previously. In principle it consists of double heated jacket vessel fitted with a filtration bottom and a mixing unit. [2]. Temperature of all dehydrating solution was set to the value of 103°C.

Course of the dehydration process was continuously observed by taking samples in 10 minute intervals. The influence of the quality of the second component of the dehydrating solution and its concentration was evaluated from the viewpoint of achieved phase composition and morphology of the resulting product by X-ray -diffraction and scanning electron microscopy.

Table 1. Composition of mixed dehydration solutions based on KCl and NaCl.

Sample label	Mixing ratio KCl : NaCl (% mass)
1	100 : 0
2	0 : 100
3	50 : 50
4	75 : 25
5	80 : 20
6	85 : 15

RESULTS AND DISCUSSION

Effect of mixing ratio between KCl and NaCl on the formation and morphology of hemihydrate

Effect of basic dehydrating solutions based on pure KCl or NaCl is illustrated in Figures 1 and 2. Figures always show X-ray analysis record and scaning electron microscopy scan (magnification 600 ×) of the sample after finishing of dehydration process or conversion to the final product in the selected dehydrating solution.

When using pure potassium chloride to prepare the model solution, gorgeyite emerged during dehydration already after 40 minutes, the condition of the product did not change even after 240 minutes.

It is apparent both from the radiogram and from the scanning electron microscopy that already after 50 minutes of dehydration the only dehydration product is the calcium sulfate hemihydrate, mineralogical bassanite. Mineralogical composition of the product did not change even by the time of last sampling after 240 minutes.

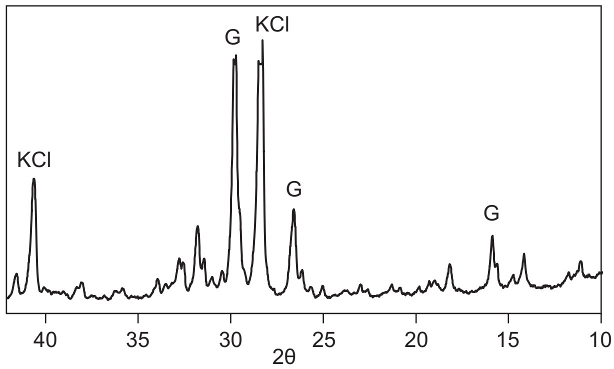
Results confirm that pure KCl solution cannot be used as dehydration medium, because instead of gypsum dehydration the primary reaction is the creation of gorgeyite double salt. A presumption was made that this phenomenon is related to the electrochemical nature of potassium ion and this process could be influenced by adding sodium ions into the dehydration solution.

Therefore, in further studies model mixing solutions with KCl and NaCl in accordance with Table 1 were prepared, see Figures 3-6.

Prepared hemihydrate indicated basically perfect concordance with the morphology of the mineral bassanite. Based on partial evaluation of results, gradual increase of KCl share in mixed solution was approached.

In mineralogical aspect, the product emerging from dehydration represented pure calcium sulfate hemihydrate, with perfect morphology of very fine-grained α-hemihydrate.

When further increasing the share of KCl, the process of gypsum transformation went ahead differently. In this solution, first the dehydration to hemihydrate occurred, which was identified already after 20 minutes, see Figure 5a. However, it gradually transformed into the mineral gorgeyite, see Figure 5b. Full transformation was observed after 240 minutes.



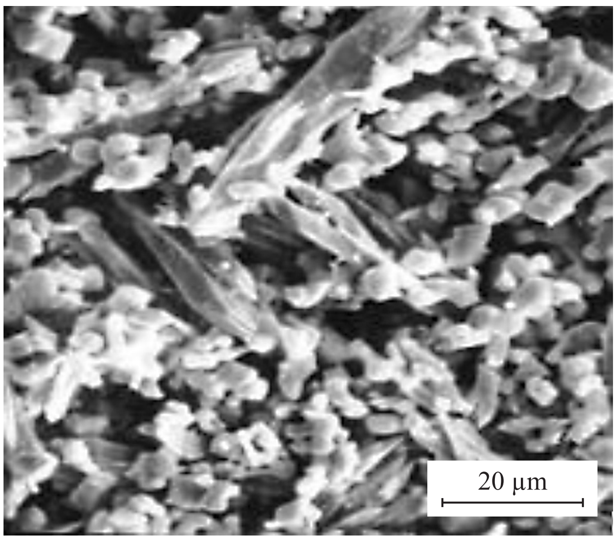


Figure 1. Sample prepared in dehydrating solution – KCl:NaCl = 100:0 taken after 40 minutes.

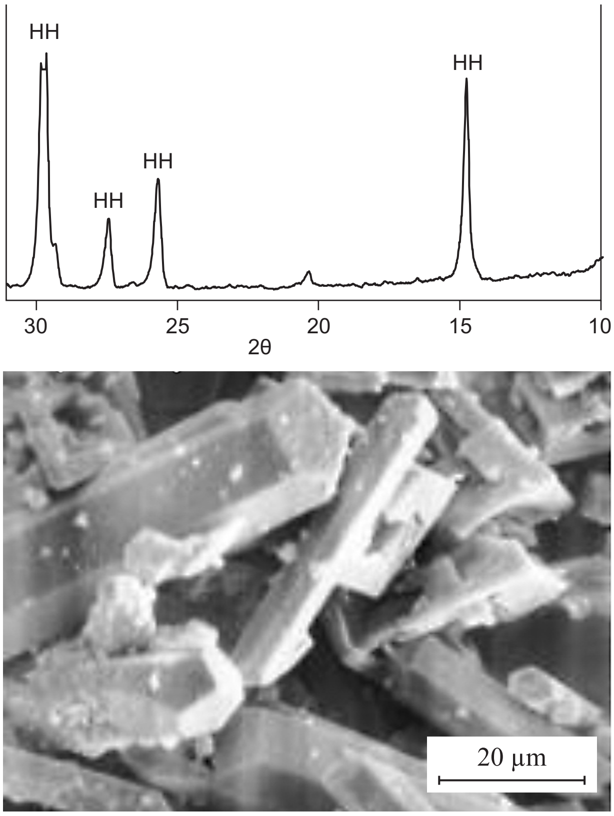


Figure 2. Sample prepared in dehydrating solution No. 2 – KCl:NaCl = 0:100 taken after 50 minutes.

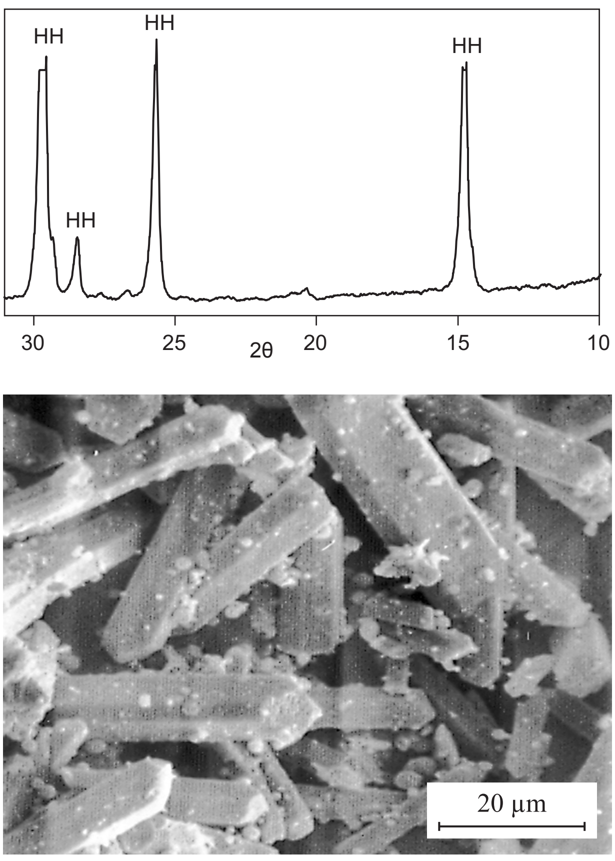


Figure 3. Sample prepared in dehydrating solution No. 3 – KCl:NaCl = 50:50 taken after 40 minutes.

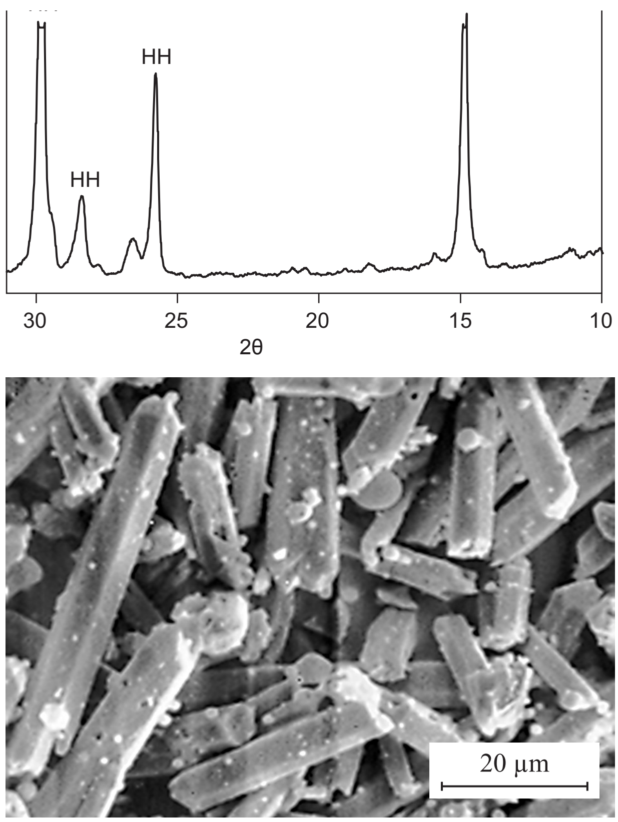


Figure 4. Sample prepared in dehydrating solution No. 4 – KCl:NaCl = 75:25 taken after 30 minutes.

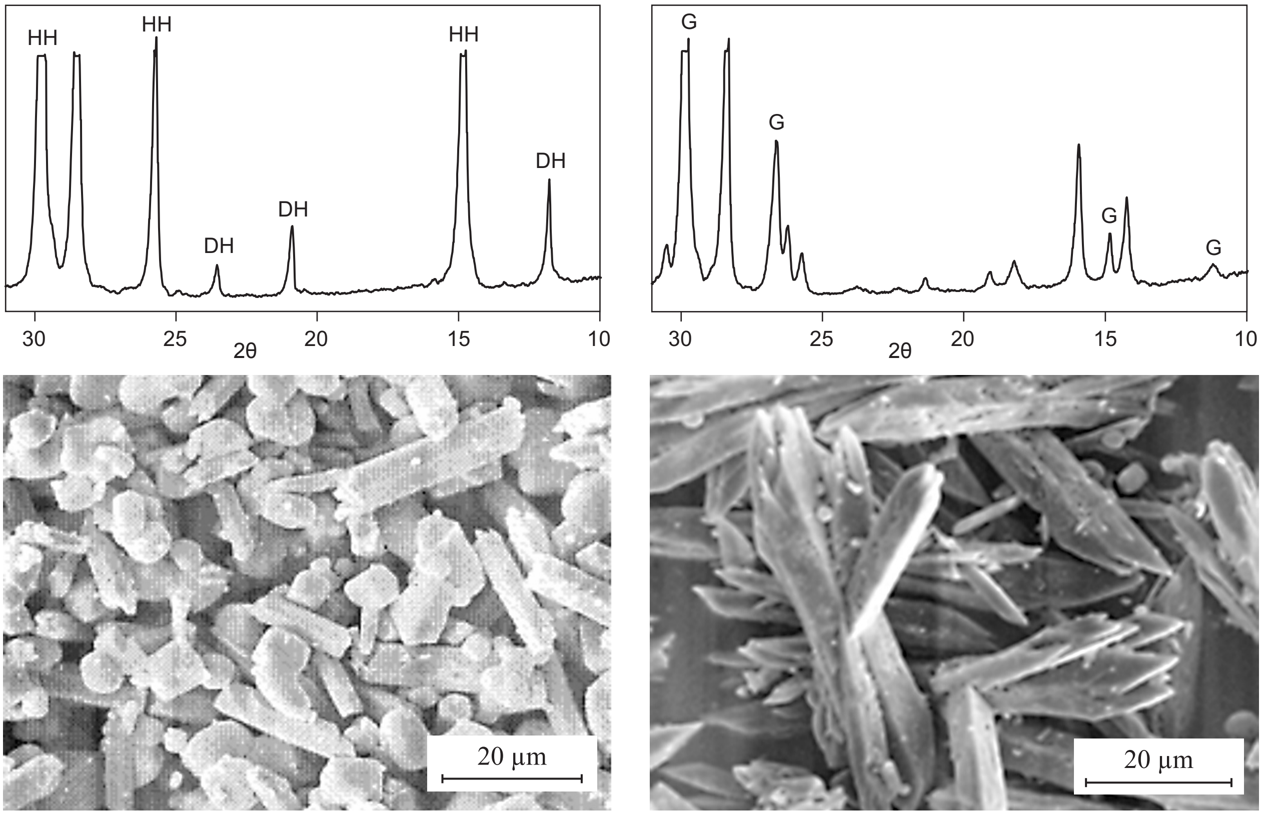
The process of gradual transformation of gypsum through hemihydrate to gorgeyite is clearly apparent on radiograms and images from scanning electron microscopy, see Figures 6a and 6b. Proportionally to the decrease of NaCl proportion, the speed of said transformation is higher than in the preceding case.

From the results it is apparent that dehydration of gypsum to alpha- hemihydrate can be effected in a mixed solution based on NaCl and KCl. This, however, must contain at least 25 % NaCl.

Effect of the mixed solution concentration on the kinetics and morphology of hemihydrate

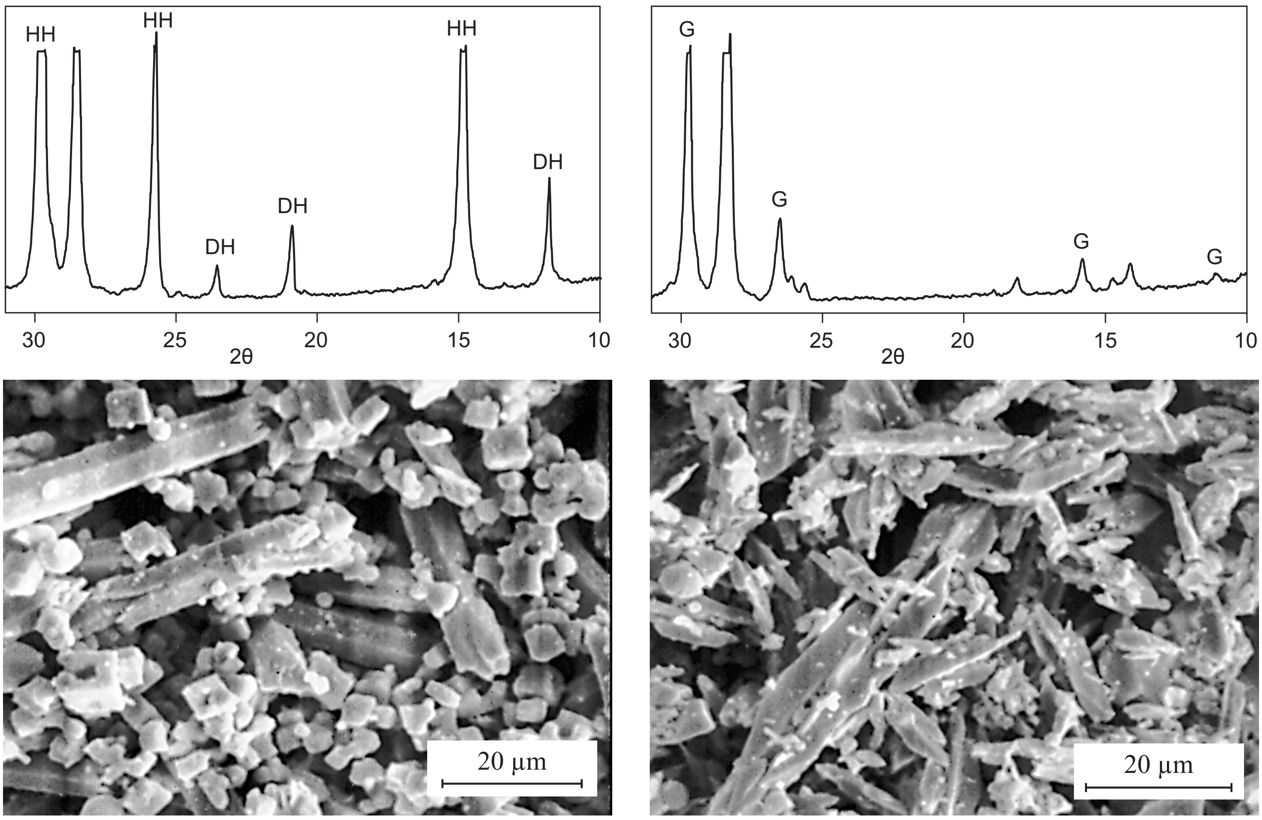
The effect of concentration was tested on the mixed solution 4 composed of 25 % NaCl and 75 % KCl, see Ttable 1, which is the most suitable from the viewpoint of the potassium chloride usability. The concentration of the mixed solution was observed in the range of 15 to 30 % mass, see Figures 7-11.

The radiogram of the sample on the Figure 7 shows the presence of a single phase, and the calcium sulfate hemihydrate. Due to the low speed of dehydration corresponds the morphology of hemihydrate to the massive, perfectly circumscribed orthorombic crystals, which can be attributed to the high quality of the alpha-hemihydrate used.



a) after 20 min.   b) after 240 min.

Figure 5. Sample prepared in dehydrating solution no. 5 – KCl:NaCl = 80:20 taken after 20 minutes (a) and 240 minutes (b).



a) after 20 min.   b) after 80 min.

Figure 6. Sample prepared in dehydrating solution no. 6 – KCl:NaCl = 85:15 taken after 20 minutes (a) and 80 minutes (b).

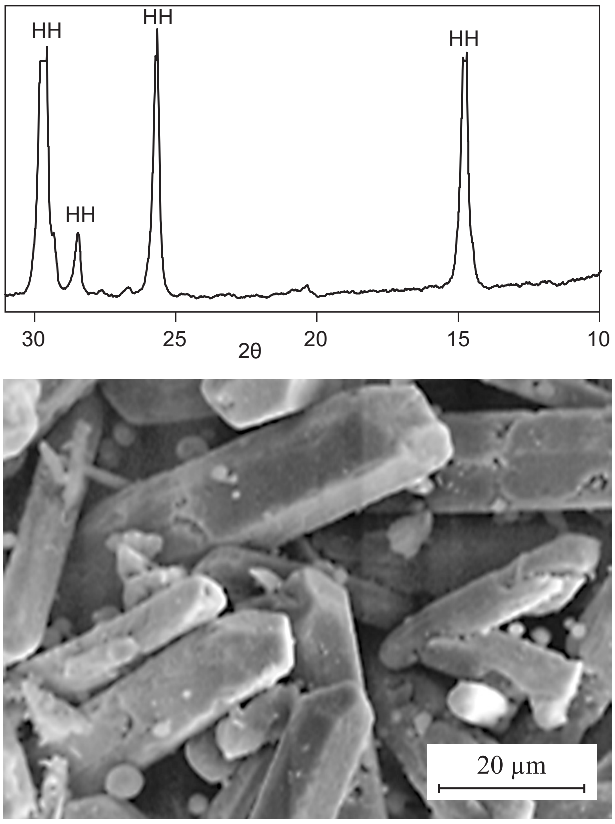


Figure 7. Sample prepared in 15 % dehydrating solution No. 4 taken after 120 minutes.

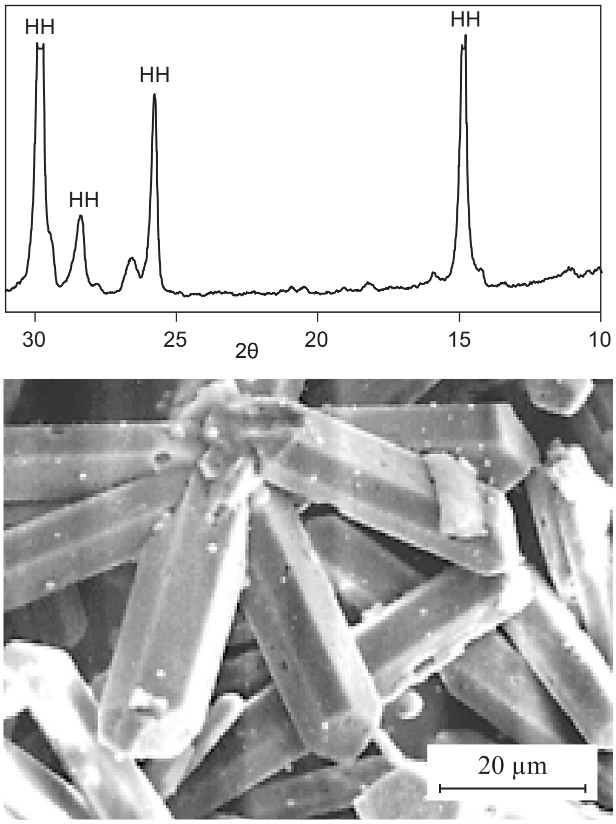


Figure 8. Sample prepared in 20 % dehydrating solution No. 4, taken after 90 minutes.

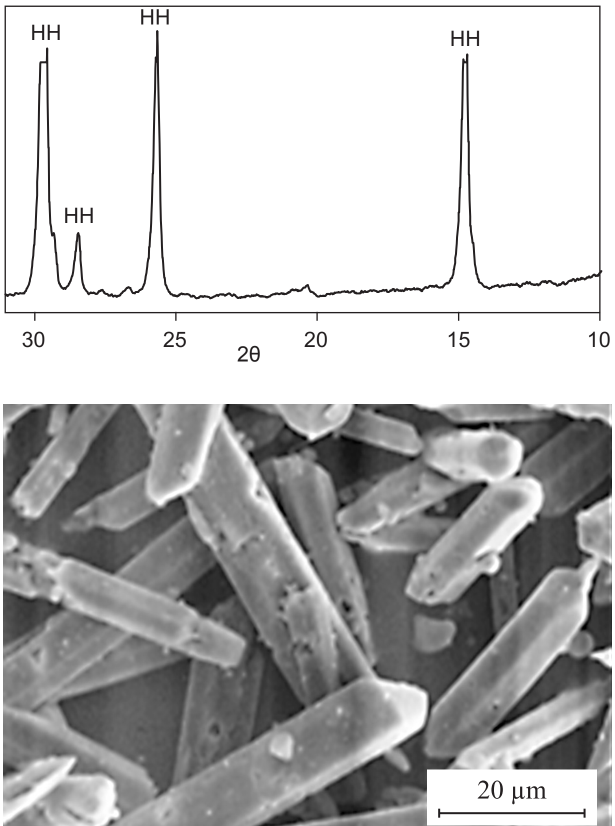


Figure 9. Sample prepared in 22 % dehydrating solution No. 4, taken after 60 minutes.

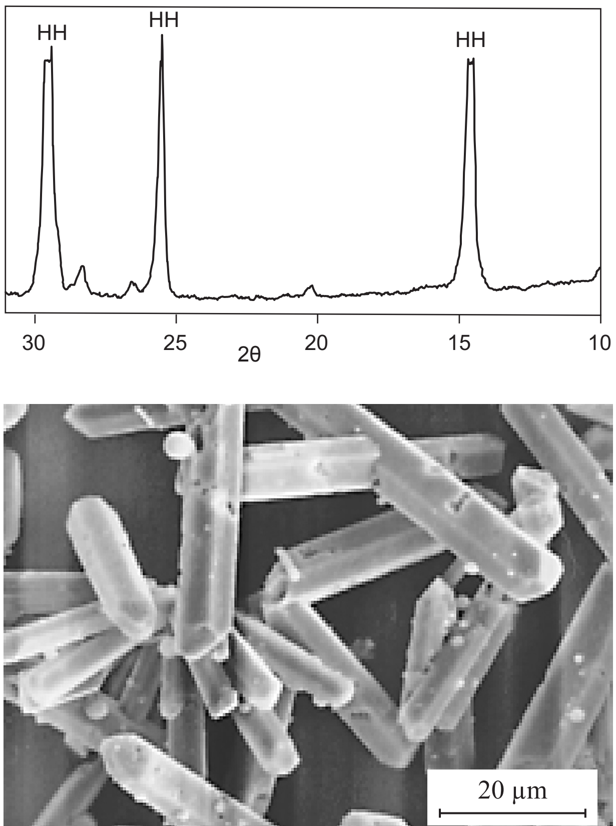


Figure 10. Sample prepared in 26 % dehydrating solution No. 4, taken after 50 minutes.

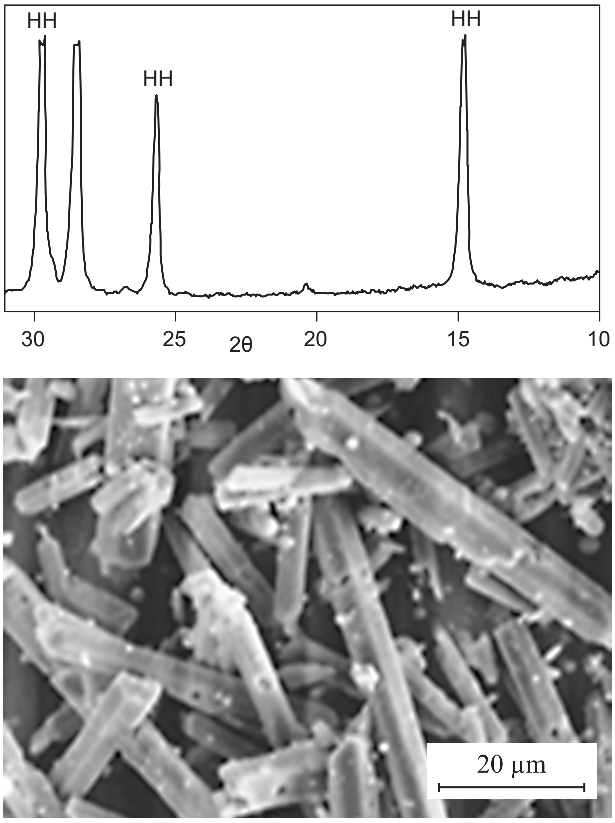


Figure 10. Sample prepared in 26 % dehydrating solution No. 4, taken after 50 minutes.

From the radiogram and directly viewing the morphology of the resulting product it is clear that this sample has very similar characteristics to the alpha-hemihydrate which was prepared in the previous mixed solution with a concentration of 15 %.

Due to the higher concentration of the mixed solution has been to increase the speed of dehydration, thereby were creating although automorfic, but finer grains.

The sample prepared by dehydration in a mixed solution of the higher concentration can be observed further reduce the size of grains of alpha- hemihydrate as a result of increasing the speed of this process.

In comparison with previous samples occurred due to penetrative dehydration kinetics further deterioration of the alpha- hemihydrate morphology. Firstly, the particles were smaller, and the secondly they were characterized as only grains hypautomorfic.

Mechanism of action of potassium chloride in the dehydration of gypsum in monitored solutions

Through gypsum dehydration tests on the basis of KCl solutions it has been confirmed that potassium chloride alone is completely unsuitable for this purpose, due to its electrochemical nature. Due to higher mobility of potassium ($7.62 \times 10^{-2} mm^2 s^{-1} V^{-1}$) [8], its ion in liquid environ of increased temperature will preferentially penetrate into the structure of calcium sulfate, where it will isomorphically substitute calcium ions during the formation of the mineral gorgeyite.

Sodium ion, in partial replacement by sodium chloride, has a lower mobility ($5.20 \times 10^{-2} mm^2 s^{-1} V^{-1}$) [8] and simultaneously a sufficiently large ionic radius (0.098 nm). Therefore, it will be completely indifferent to potential ion substitutions and will thus, after reaching the minimum critical concentration, decrease the proportion of potassium ions substituting calcium below the thres-hold needed to create gorgeyite.

The condition, in which the critical proportion of sodium ions is achieved, may be considered to be the mixed solution containing 80 % mass KCl and 20 % mass NaCl. Here, first the dehydration of gypsum was observed, which then, prior to termination of the test, transformed into formation of gorgeyite. It may be said that in this case the gradual increase of the frequency of substituted potassium ions in the structure of calcium sulfate occurred under very low representation of sodium ions, while limit values necessary for creation of gorgeyite have been achieved still during the unfinished dehydration of gypsum to hemihydrate.

CONCLUSION

It was proven through conducted tests that potassium chloride present in dusts alone is unusable for dehydration of gypsum in chemically pure form, because simultaneously with this process the competitive process of gorgeyite creation occurs at a much higher reaction velocity due to the electrochemical nature of potassium ions. Sodium ions decrease the reaction velocity of goregyite formation, thus creating the premise for gypsum hydration to hemihydrate. Through substantial ionic radius and lower mobility they stall the transport of potassium ions, thus decreasing the velocity of their substitution for calcium ions.

The mass concentration of dehydration solution of 20 % may be considered as optimal for mixed dehydration solution containing 75 % of potassium chloride and 25 % of sodium chloride. Further research should aim at the optimization of solution's concentration to the lowest technically usable level allowing to achieve the most suitable morphology of obtained α-plaster. Only under this condition the low dehydration velocity will allow for creation of massive, well crystallographically defined grains, which are a precondition for low dose of mixing water and thus the main condition for achieving the highest possible strength.

Acknowledgement

All work has been supported by GP103/08/P231, FR-TI2/653 and FAST-S-12-25/1671.

References

1. Fridrichová, M., Kalivoda K., Dvořák K. in: Proc. Conference Maltoviny, p. 238 – 245, Vysoké učení technické v Brně, Brno 2008.
2. Dvořák K.;, Fridrichová M.; M., Gazdič D.: Possibilities of alpha gypsum preparation in chloride salt solutions. Advanced Materials Research. Vol. *598*, 310 (2012) pp 310-313 ISSN 1022-6680.
3. Baohong Guan, Li Yang, Hailu Fu, Bao Kong, Tingying Li;, Liuchun Yang: α-calcium sulfate hemihydrate preparation from FGD gypsum in recycling mixed salt solutions, Chemical Engineering Journal *(October 2011), 174*, (1), pg. 296-303 (2011).
4. Bradna P.: Sádry 2009. http://che1.lf1.cuni.cz/html/Sadry_2009_cz.pdf
5. Fridrichová, M., Havlíčková Š., Zlámal P., Dvořák K. in: 16.ibausil 1 *897* (2006).
6. Baohong Guan, Guangming Jiang, Zhongbiao Wu, Jingwei Mao, Bao Kong: Preparation of α-Calcium Sulfate Hemihydrate from Calcium Sulfate Dihydrate in Methanol–Water Solution under Mild Conditions, Journal of the American Ceramic Society *Volume 94*, Issue 10, pages 3261–3266, October (2011).
7. Liuchun Yang,; Zhongbiao Wu;, Baohong Guan;, Hailu Fu,; Qingqing Ye: Growth rate of α-calcium sulfate hemihydrate in K–Ca–Mg–Cl–H_2O systems at elevated temperature, Journal of Crystal Growth *311* 4518 ((October 2009), 311 (20), pg. 4518-4524.
8. Moore W. J.: Fyzikální chemie, p. 447, SNTL Praha 1981., pg. 447