

ACCUMULATION OF ALKALIS IN THE RECYCLING FILTRATE OF THE PHOSPHOGYPSUM PULPS

#ANTANAS KAZILIUNAS, MARYTE BACAUSKIENE

*Institute of Architecture and Construction at Kaunas University of Technology
Tunelio 60, LT-44405, Kaunas, Lithuania*

#E-mail: kaziliunas.antas@gmail.com

Submitted March 3, 2011; accepted September 26, 2011

Keywords: Phosphogypsum, Filtrate, Recycle, Alkalis

Sodium and potassium combinations existing in phosphogypsum are highly soluble and remain in the filtrate, their amount increasing with each recycle. It has been determined that the amount of alkalis in the recycling filtrate depends on an amount of alkalis in uncleaned phosphogypsum, a number of recycles in the filtrate, the technology of the phosphogypsum pulp preparation and an amount of soluble phosphates. New phosphate formations composed in an acid medium (pH = 4.5-5) are well crystalized crystals. They do not alter the filtrability of the phosphogypsum pulp. The new combinations formed in an alkaline medium (pH = 7-11) are colloidal. They settle down on the surface of the hard particles and make the filtration of the phosphogypsum pulp complicated. The filtrated phosphogypsum is more humid which causes the growth of the amount of alkalis carried out together with moisture and thus the lower alkali concentration is observed in the recycling filtrate. In the discussed case, the larger amount of soluble phosphates of uncleaned phosphogypsum is formed the larger amount of the colloidal particles in the neutralized phosphogypsum pulp which results in complicated filtration. In all the cases, the alkali concentration in the recycling filtrate approaches the maximum degree which would take place if alkalis existing in uncleaned phosphogypsum were thawed in humidity of cleaned phosphogypsum.

INTRODUCTION

Acid phosphorus and fluorine impurities that are formed in phosphogypsum have a deteriorating effect on the properties of the gypsum binder [1, 2, 3, 4, 5]. These impurities are eliminated by washing phosphogypsum with water or the solution of citric and other acids, screening the smallest particles and by neutralizing the impurities with $\text{Ca}(\text{OH})_2$, CaCO_3 , K_2CO_3 , KOH , portland cement, NH_4OH and other materials [5, 6, 7, 8, 9]. Sensitivity to lime is an essential characteristics of phosphogypsum [3, 4]. The least water-soluble phosphate combinations are calcium orthophosphates of the hydroxylapatite group $\{\text{Ca}_5(\text{PO}_4)_3\text{OH}\cdot n\text{H}_2\text{O}$ or $\text{Ca}_3(\text{PO}_4)_2\cdot m\text{H}_2\text{O}\}$. They are formed when phosphogypsum is strewn into lime suspension, the alkaline medium is kept in the pulp and neutralization is completed at $\text{pH} = 7-11$. The phosphate combinations of low water solubility, i.e. dihydrate calcium hydrophosphates ($\text{CaHPO}_4\cdot 2\text{H}_2\text{O}$), are formed when the neutralization process is completed at $\text{pH} = 4.5-5$ [8, 11]. The composed apatites are colloidal, and calcium hydrophosphates are crystals [11]. During the neutralization reactions water soluble fluorides are bound into non-soluble calcium fluorides when the liquid phase is $\text{pH} = 3-4$. In all the above mentioned

phosphogypsum cleaning technological processes (i.e. when phosphogypsum is washed with water, impurities dissolved or neutralized) a large amount of water is utilized. To diminish water input the filtrate of the phosphogypsum pulp is sent back for the preparation of another pulp. Sodium and potassium combinations existing in phosphogypsum are highly soluble and remain in the recycling filtrate after washing or neutralization operations, their amount increasing with each recycle. The alkalis modify the solubility of materials and thus may have an impact on the technological process, the properties of an obtained product and to save of environment. The paper aims at the determination of the intensiveness of alkali accumulation in a recycling filtrate and the description of the particular factors causing it.

EXPERIMENTAL

Phosphogypsum-dihydrate made of the Kola apatite was used for investigation. The chemical structure of phosphogypsum (calculated for the dry product) was, in %: $\text{CaO} - 32$; $\text{SO}_3 - 40.5$; $\text{SiO}_2 - 0.4$; $\text{R}_2\text{O}_3 - 1.3$; $\text{Na}_2\text{O} - 0.24$; $\text{K}_2\text{O} - 0.04$; P_2O_5 total - 1.5; P_2O_5 water soluble - 1.09; F total - 0.14; F water soluble - 0.05;

H₂O - 19,8. The phosphogypsum moisture was 19 %; density was 750-800 kg/m³; the specific surface (measured by the air permeability method) was 270 m²/kg. To prepare lime suspensions the reagent CaO was used. Other materials used in the experiment were chemically clean.

The neutralization of the phosphogypsum impurities was carried out according to [11]. For half an hour, 0.5 kg of phosphogypsum had been strewn into the lime suspension mixed in the reaction vessel. After 10 minutes of additional mixing, for 5 minutes the neutralized phosphogypsum pulp had been filtrated with the vacuum cleaner through the filtrating paper (white tape). For the preparation of the first lime suspension the drinking urban water-supply water was used. The filtrated phosphogypsum pulp filtrate was used for the preparation of another lime suspension and neutralization of phosphogypsum impurities. To prepare lime suspension the amounts of water and recycling filtrate were determined by the calculation of the desired ratio of dry phosphogypsum/liquid phase (F/L), in the phosphogypsum pulp. The amount of lime was calculated stehiometrically, the amount necessary for the formation of calcium orthophosphate and for binding soluble fluoride into insoluble calcium fluoride. For the formation of calcium orthophosphates of the apatite group {Ca₅(PO₄)₃OH·nH₂O or Ca₃(PO₄)₂·mH₂O}, neutralization was completed when in the phosphogypsum pulp pH = 11 and 7, accordingly). For the formation of dihydrate calcium hydroorthophosphate (CaHPO₄·2H₂O), neutralization was completed when the pulp's pH = 4.5-5. The alteration of the pulp's pH was uninterruptedly controlled by ionometer EV-74. After the filtration of the pulp the alkali concentration in the filtrate was measured. The filtrate was used in the following cycle of lime suspension preparation and phosphogypsum neutralization. The concentration of alkalis in the filtrates

was found out with the flame photometer ATS 200S. The surface of the neutralized phosphogypsum particles was scanned with the nuclear power microscope DualScope™ C-26. The humidity of phosphogypsum was determined by its drying at 50° C temperature.

RESULTS AND DISCUSSION

The accumulation of alkalis in the acid and alkaline mediums of the recirculation filtrates in the phosphogypsum pulps is shown in Figure 1 and Figure 2.

Figure 1 shows the accumulation of alkalis in the recycling filtrates when phosphogypsum neutralization was completed in an acid medium of the pulp (pH = 4.5-5). The curves demonstrate that in the recycling filtrates alkalis accumulate more intensively when the ratio of the recycling filtrate and phosphogypsum (F/L) decreases in the neutralized acid phosphogypsum pulps. With the increase of the number of the phosphogypsum pulp neutralization and filtration cycles this difference gradually grows, and the alkali concentration in the recycling filtrates approaches certain limits.

A similar alkali accumulation tendency is also seen in the mildly alkaline recycling filtrates when the process of phosphogypsum neutralization was completed at the pulp's pH = 7-11. However, in this case, the limit approached by the concentration of the accumulated alkalis in the recycling filtrates is lower than the alkali concentration in the phosphogypsum pulps whose neutralization was completed in an acid medium.

To find out the reasons for the difference in the alkali accumulation in the phosphogypsum pulps whose neutralization was completed in the acid and alkaline medium, the surfaces of the phosphogypsum particles neutralized in the acid and alkaline medium were scanned with the nuclear power microscope. The surface of the

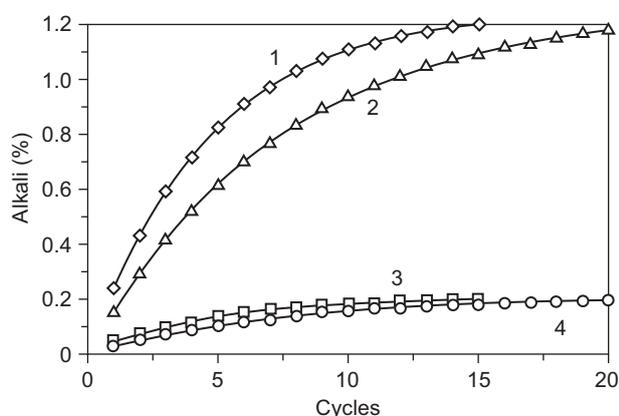


Figure 1. Alkali (Na₂O - curves 1 and 2; K₂O - curves 3 and 4) accumulation in the recycling acid filtrates (pH = 4.5-5). Dry phosphogypsum and liquid phase ratio (F/L) in the phosphogypsum pulp: F/L = 1 - curves 1 and 3; F/L = 1.5 - curves 2 and 4.

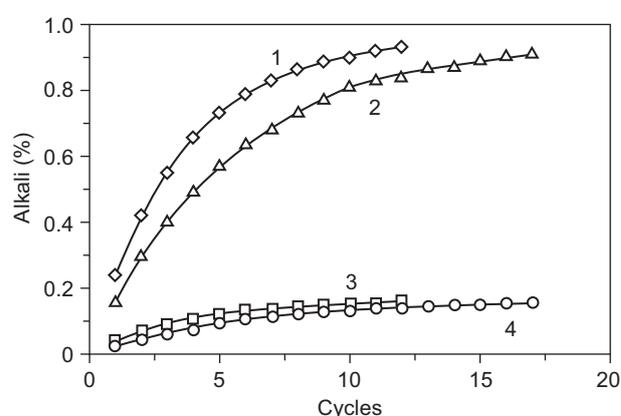


Figure 2. Alkali (Na₂O - curves 1 and 2; K₂O - curves 3 and 4) accumulation in the recycling alkaline filtrates (pH = 7-11). Dry phosphogypsum and liquid phase ratio (F/L) in the phosphogypsum pulp: F/L = 1 - curves 1 and 3; F/L = 1.5 - curves 2 and 4.

particles of phosphogypsum neutralized in a mildly acid medium is clean, and on it the edges of the crystal formation are clearly seen (Figure 3).

The earlier experiments which aimed at the determination of the calcium phosphate formation in the alkaline and acid medium [11] resulted in finding out that in a mildly acid medium (pH = 4.5-5) well crystallized dihydrate calcium hydroorthophosphates (CaHPO₄·2H₂O) are composed. By their size and shape they are similar to the phosphogypsum crystals. As the common view given in Figure 3 shows, they do not settle on the surface of the phosphogypsum particles and thereby do not alter the filtrability of the phosphogypsum pulp.

The conglomeration of the fine particles between the edges of crystal formation are seen on the surface of the particles of phosphogypsum neutralized in an alkaline medium (Figure 4).

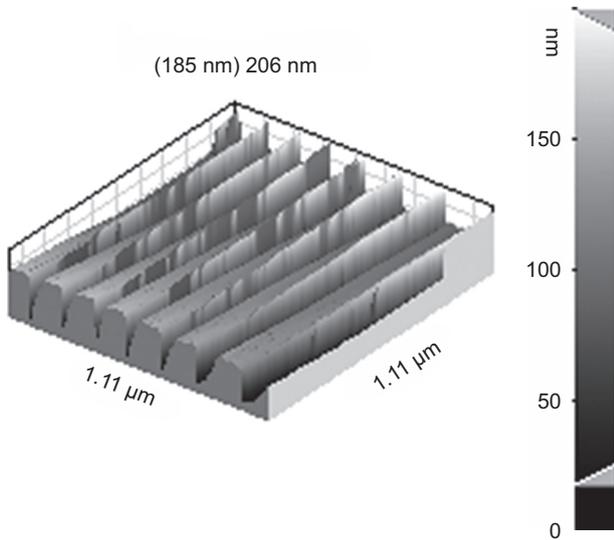


Figure 3. Common view of the particles of phosphogypsum neutralized in an acid medium (pH = 4.5-5).

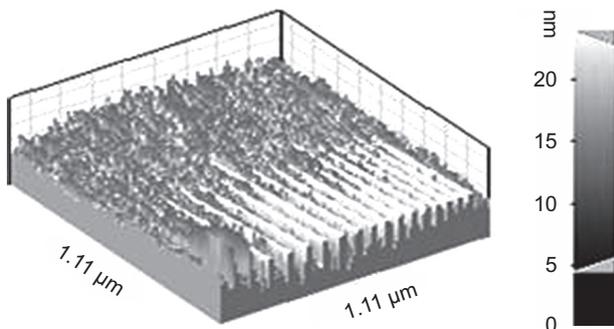


Figure 4. Common view of the surface of the particles of phosphogypsum neutralized in an alkaline medium (pH = 7-11).

As the common view given in Figure 4 shows, calcium orthophosphates of the hydroxylapatite group {Ca₅(PO₄)₃OH·nH₂O and Ca₃(PO₄)₂·mH₂O} are extremely fine and colloidal. Such conglomerations of the fine particles worsen the filtrability of the phosphogypsum pulp.

For the comparison of the phosphogypsum pulp filtrability, the washing pulps and the pulps of various neutralization degree were prepared, in which dry phosphogypsum and liquid phase ratio was F/L = 1. The impact of the amount of soluble phosphates on the filtrability of the phosphogypsum pulps has also been examined. Three phosphogypsum pulps with a larger amount of soluble P₂O₅ and an adequate amount of orthophosphorus acid mixed into uncleaned phosphogypsum were prepared. The humidity of phosphogypsum after the filtration of the variously prepared phosphogypsum pulps is given in Figure 5.

A different view is seen when the phosphogypsum pulp neutralization is completed in an alkaline medium (pH = 7-11). In this case, the pulp filtrability is worsened and humidity of filtrated phosphogypsum is higher. When the amount of soluble P₂O₅ in uncleaned phosphogypsum is increased, the filtrability of the pulps of phosphogypsum neutralized in an alkaline medium is worsened even more, since more humidity is accumulated in it (columns 5 and 6; Figure 5).

From the data presented in Figure 5 it is clear that the humidity of filtrated phosphogypsum differs very inconsiderably when the filtrated pulps were prepared only with water or neutralized until pH = 4.5-5. In this case, the amount of soluble phosphates in uncleaned phosphogypsum (when it was washed with water or neutralized until pH = 4.5-5) does not have any impact on the pulp filtrability. The humidity of cleaned phosphogypsum remains nearly the same (columns 1, 2, 3, 4; Figure 5).

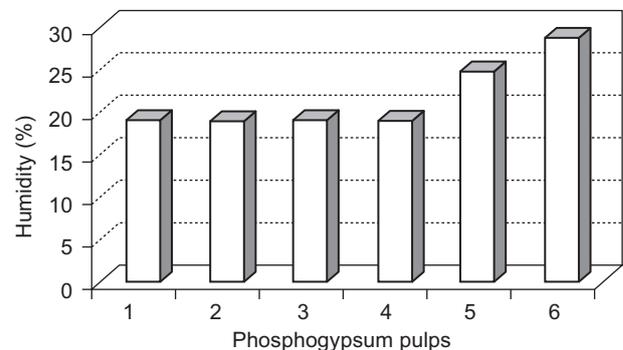


Figure 5. Phosphogypsum humidity after the filtration of the variously prepared phosphogypsum pulps (F/L = 1). Columns 1, 2 - washing; columns 3, 4 - neutralization in lime suspension until pH = 4.5-5; columns 5, 6 - neutralization in lime suspension until pH = 7-11. Amount of soluble P₂O₅ in uncleaned phosphogypsum - 1, columns 3 and 5 - 1.1 %; columns 2, 4 and 6 - 1.6 %.

After the analysis of the determined regularities it was found out that, generally, after an adequate number of recycles the alkali concentration in the recycling filtrate may be calculated on the basis of the following deduced empiric equations, in which m is alkali amount in uncleaned phosphogypsum (%); F/L - expresses dry phosphogypsum and liquid phase ratio; F is dry phosphogypsum amount in the pulp (kg); L is liquid phase amount in the pulp (l. $L = W + t \cdot F$); W is water (i.e. in the first pulp) or the recycling filtrate amount utilized for the pulp preparation (l); t is uncleaned phosphogypsum humidity (%); h - expresses cleaned phosphogypsum humidity (after the pulp filtration - %).

The alkali concentration in the filtrate after the first cycle (%):

$$c_1 = \frac{mF}{\left(\frac{W+tF}{F}\right)F} = \frac{mF}{W+tF} = \frac{mF}{L} = m \frac{F}{L}$$

After the second cycle (%):

$$c_2 = \frac{mF + c_1(L - hF)}{\left(\frac{W+tF}{F}\right)F} = \frac{mF + \frac{mF}{L}(L - hF)}{L} = \frac{mF}{L} + \frac{mF + (L - hF)}{L^2} = m \frac{F}{L} \left(1 + \frac{L - hF}{L}\right)$$

After the third cycle (%):

$$c_3 = \frac{mF + c_2(L - hF)}{\left(\frac{W+tF}{F}\right)F} = \frac{mF + \left[\frac{mF}{L} + \frac{mF(L - hF)}{L^2}\right](L - hF)}{L} = \frac{mF}{L} + \frac{mF(L - hF)}{L^2} + \frac{mF(L - hF)^2}{L^3} = m \frac{F}{L} \left[1 + \frac{L - hF}{L} + \frac{(L - hF)^2}{L^2}\right]$$

After then n^{th} cycle (%):

$$c_n = m \frac{F}{L} \left[1 + \frac{L - hF}{L} + \frac{(L - hF)^2}{L^2} + \dots + \frac{(L - hF)^{n-1}}{L^{n-1}}\right]$$

As it is seen from the curves given in Figure 1 and Figure 2 and the deduced formula, with the increase of the number of the filtrate recycles the alkali concentration in the recycling filtrate asymptotically approaches to the maximum:

$$c_{\max} = \frac{m}{h}$$

i.e. the maximum concentration of alkalis that would take place if alkalis existing in uncleaned phosphogypsum were thawed in the humidity of cleaned phosphogypsum.

CONCLUSIONS

1. The amount of alkali accumulation in the recycling filtrates of the phosphogypsum pulps depends on the amount of alkalis in uncleaned phosphogypsum and on the number of recycles. The impact of water soluble phosphates depends on the technology of the phosphogypsum pulp preparation and is related with pulp filtrability.
2. New combinations formed during the phosphogypsum neutralization in an acid medium (pH = 4.5-5) are large in size and they do not modify pulp filtrability.
3. New formations in an alkaline medium (pH = 7-11) are colloidal and they complicate the filtration of the phosphogypsum pulp. Such phosphogypsum is more humid. In it, the amount of alkalis carried out due to humidity increases and a lower alkali concentration in the recycling filtrate is settled. Due to the increase of the amount of soluble phosphates the number of the colloidal particles increases after neutralization which complicates the filtration of the pulp.
4. The alkali concentration in the recycling filtrate approaches the maximum degree which would take place if alkalis existing in uncleaned phosphogypsum were thawed in humidity of cleaned phosphogypsum.

References

1. Tayibi H., Choura M., Lopez A.F., Alguacil J.F., Lopez-Delgado A.L.: *Journal of Environmental Management* 90, 2377 (2009).
2. Singh M.: *Cem. Concr. Res* 33, 1363 (2003).
3. Wirsching F.: *Mater. Constr.* 11, 62 (1978).
4. Beretka J.: *J. Chem. Techn. Biotechn.* 32, 607 (1982).
5. Lutz R.: *Zem.- Kalk - Gips* 12, 98 (1994).
6. Singh M.: *Cem. Concr. Res.* 32, 1033 (2002).
7. Wirsching F.: *TIZ - Fachberichte Rohstoff-Engineering* 105, 382 (1981).
8. Stonis S., Kaziliunas A., Bacauskiene M.: *Building Materials* 3, 9 (1984) (in Russian).
9. Potgieter J.H., Potgieter S.S., McCrindle R.I., Strydom C.A.: *Cem. Concr. Res.* 33, 1223 (2003).
10. Beretka J., Douglas N., King A.: *J. Chem. Techn. Biotechn.* 31, 151 (1981).
11. Kaziliunas A., Leskeviciene V., Vektaris B., Valancius Z.: *Ceramics-Silikaty* 50, 178 (2006).