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Waste Materials in Construction: Putting Theory into Practice

PROCESSING AND APPLICATION OF PHOSPHORIC GYPSUM

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ABSTRACT

In the Rotterdam Port Area in the Netherlands two phosphoric acid producers are situated. Together they produce approximately 1,8 million tons per year of phosphoric gypsum which is up till now discharged in the Nieuwe Waterweg and the North Sea.

This phosphoric gypsum is to a certain extent contaminated with the impurities of P_2O_5, F, organic matter, Radium, ect.

Research has been established into different applications of this gypsum. Phosphoric rock selection, the BAT process and purifying the gypsum result in a gypsum which could in the future replace natural gypsum in several applications.

The findings of the purification trials and proposed pilot plant along with a specification of the purified material are presented in this paper.

Keywords: phosphogypsum, applications

Introduction

At the production of phosphoric acid the residue gypsum is generated, called phosphoric acid gypsum, or also phosphoric gypsum for brevity's sake. Kemira Agro Pernis B.V. and Hydro Agri Rotterdam B.V. in Rotterdam and in Vlaardingen have a yearly production of 1.05 and 0,8 million tons of phosphoric gypsum respectively. This gypsum has up till now been discharged into the Nieuwe Waterweg and the North Sea.

Within the scope of the expiring of the licence for the discharge of phosphoric gypsum by these companies, research has been established into different applications of this gypsum.

Processes

Both phosphoric acid producers are situated in the Rotterdam Port Area and have so called wet processes.

Hydro Agri Rotterdam has a hemidihydrate Double Filter process which is shown in figure 1.

Kemira uses the Nissan-H Repulp process shown in figure 2.

In the wet phosphoric acid proces the phosphate rock is digested with sulfuric acid. The resulting gypsum is then filtrated. Apart from the phosphoric acid also a 28 percent Silicon Fluorine Solution is extracted. Both processes have a very high efficiency (98-99%) and belong to the B.A.T. processes.

Experimental

Characterization of phosphogypsum

The two phosphogypsums were characterized for various chemical constituents. See table 1.

Purification of phosphogypsum

radioactivity aspects. In order to purify the gypsum a fundamental research[1] was conducted into the appearance of the Radium in the rock and the gypsum. The phosphate rock was digested with nitric acid. The residu and the gypsum then produced was analyzed using a scanning electron microscope.

hydrocyclone tests. Phosphogypsum and water, in the proportion 1:3 by volume was thoroughly mixed in a mixer slurry tank. After attaining uniformity in the gypsum slurry the fine fraction (< 15 μm) was removed using a one-stage hydrocyclone. Under and overflow samples were collected. The water was removed by decantation and filtration. The gypsum samples were analyzed for various constituents.

Results and discussion

radioactivity aspects. From a literature survey it was found that there are very little publications on the appearance of Radium in both phosphate rock and gypsum[2]. In the phosphate rock few relatively big (50 μm) particles containing Strontium and Barium were found (photo 1).
In the gypsum the Sr/Ba containing particles were different in shape and smaller (photo 2).
On the basis of a existing relation[2] between Sr/Ba and Ra it is proved that radium is already present in solid particles in the phosphate rock. Further research is focussed on the different appearance of the Radium in the phosphate rock and the verification of the relationship between Sr/Ba and Radium containing particles.

hydrocyclone tests. The analyses of the samples, purified by hydrocyclone treatment are reported in table 3.
From this result it can be seen that the samples collected at the bottom, i.e. underflow, had a comparitively lower level of Radium. The underflow samples were also more white which is probably caused by the removal of the organic matter by the hydrocycloning[3].
In the overflow less than 5% by weight of the total feed solids were found. The results are in line with the literature[2].

proposed pilot plant for the purificatin of phosphogypsum

Based on the results obtained a pilot plant for the purification of phosphogypsum of the capacity of 5 ton/h has been proposed (see figure 3). In this pilot plant the impure phosphogypsum shall be mixed with water. In the mixing tank the solid content is reduced to ± 10% m/m. This slurry is pumped to a one stage hydrocyclone set. In the hydrocyclone the fine fraction (< 15 μm) of the gypsum is preferentially removed to lower the radioactivity concentration. The underflow will contain ± 55% m/m solids.

The pH of the underflow in the mixing tank will be increased to 5 using lime. On the vacuum belt filter the gypsum is washed with water to remove soluble salts. The upgraded, washed and dewatered gypsum is than ready for calcination.

specifications of the purified phosphogypsum

On the basis of the research specifications for the purified phosphogypsum have been worked out. They are however based on the following conditions:

- use of selected phosphate rock types;
- best available technique for phosphoric acid production;
- purification and dewatering of the gypsum.

In table 3 the specification for the purified phosphogypsum is given.

Conclusions

1. Phosphogypsum can be purified using hydrocyclones. The research showed that the organic matter and Radium can be reduced considerably by this treatment.
2. Based on phosphate rock selection, a BAT phosphoric acid process and a purification treatment a gypsum can be produced which can be compared with natural gypsum.
3. A pilot plant of the capacity of 5 ton/hour is likely to be fabricated and installed by the end of this year.

References

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3. A Singh et.al., „An improved process for the purification of phosphogypsum", Construction and Building materials, 1996, vol.10, no. 8, 597-600.

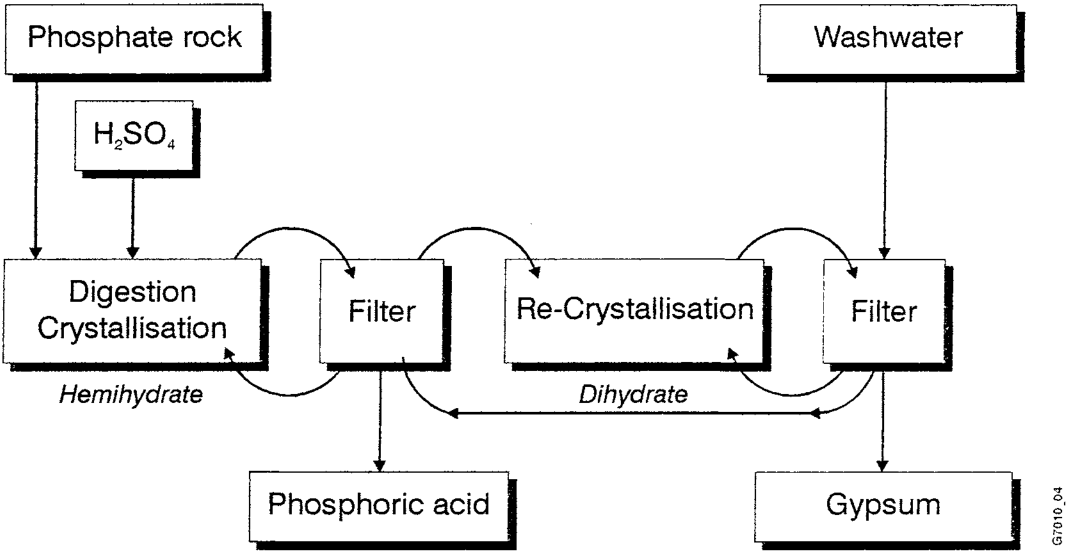

Figure 1. Hemidihydrate Double filter Process from Hydro Agri Rotterdam

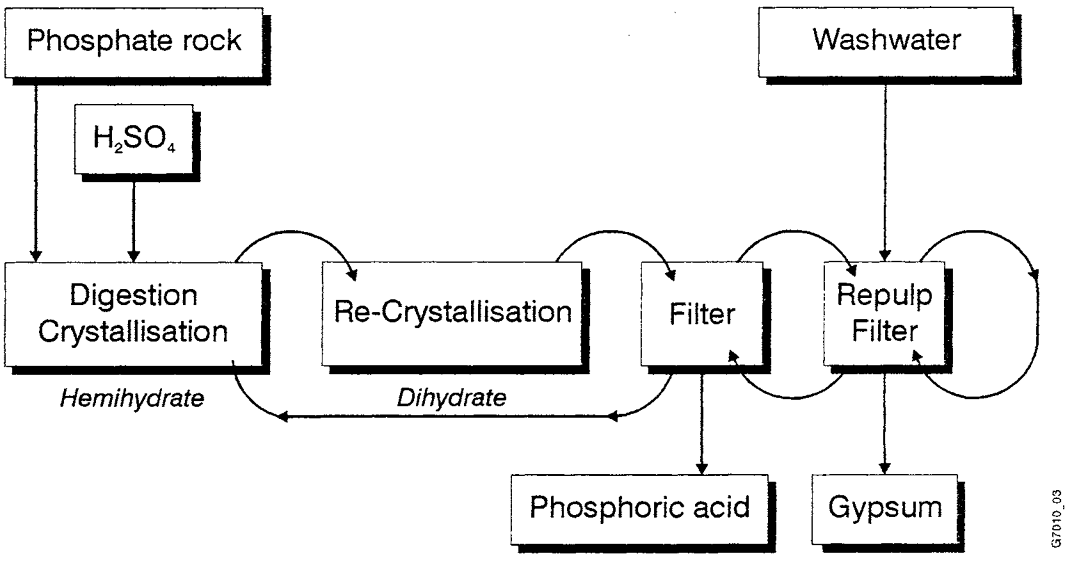

Figure 2. Nissan-H Repulp Process

Flowsheet Gypsum Upgrading Unit

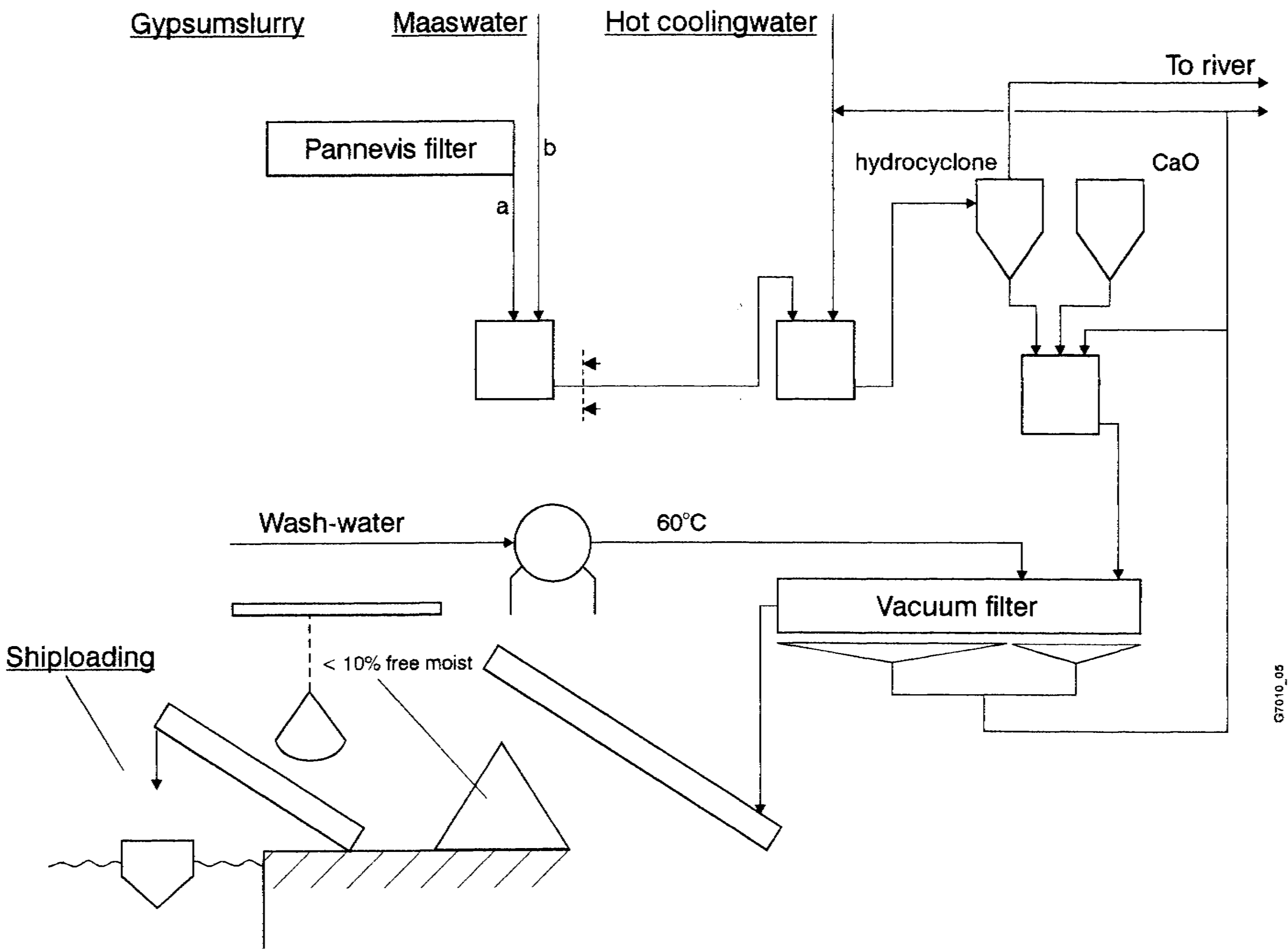

Table 1. Chemical analysis of the two phosphogypsums

Constituents		Kemira Agro dihydrate gypsum	Hydro Agri dihydrate gypsum
CaO	%	32	32
		(97-98% $CaSO_4 2aq$)	(97-98% $CaSO_4 2aq$)
P_2O_5	%	0,45	0,1
SiO_2	%	1,2	0,8
Al_2O_3	%	< 0,1	< 0,1
Fe_2O_3	%	< 0,01	< 0,01
F (tot)	%	0,5	1,0
Cd	mg/kg	< 0,5	< 0,5
Hg	mg/kg	0,08	0,09
As	mg/kg	< 0,5	< 0,1
Pb	mg/kg	1,6	1,5
Ni	mg/kg	0,5	< 0,5
Zn	mg/kg	2,5	< 0,5
Cr	mg/kg	1,2	1
Cu	mg/kg	5	< 0,5
Ra-226	Bq/kg	500	450
Th-232	Bq/kg	25	< 8

Table 2. Analyses of phosphogypsum before and after hydrocyclone purification

Sample		Before	After (underflow)
Radium	Bq/kg	490	284
Thorium	Bq/kg	15	13

Table 3. Upgraded synthetic gypsum

Parameter	Formula	Unit	Value
1. Free Moisture	H_2O	Wt%	< 10
2. Calcium Sulphate	$CaSO_4*2H_2O$	Wt%	> 97
3. pH value	pH		> 5
4. Colour			White
5. Odour			neutral
6. Magnesium oxide, water solube	MgO	Wt%	< 0,1
7. Sodium oxide, water soluble	Na_2O	Wt%	<0,1
8. Potassium oxide, water soluble	K_2O	Wt%	< 0,02
9. Chloride	Cl	Wt%	< 0,01
10. Toxicity			non-toxic
11. Organic substances			2)
12. Phosphorus pentoxide, total	P_2O_5	Wt%	< 0,3
13. Phosphorus pentoxide, water soluble	P_2O_5	Wt%	< 0,01
14. Fluoride, total	F	Wt%	< 0,5
15. Fluoride, water soluble	F	Wt%	< 0,03
16. D_{50}		µm	> 60
17. Cd	Cd	mg/kg	< 1
18. Heavy Metals (E Pb, Cr, Ni, As, Cu, Zn, Hg)		mg/kg	< 10
19. Radium		Bq/kg	< 120
20. Thorium		Bq/kg	< 20
21. Kalium		Bq/kg	< 10

2) actual value to be specified but will have no negative impact on setting time and/or colour

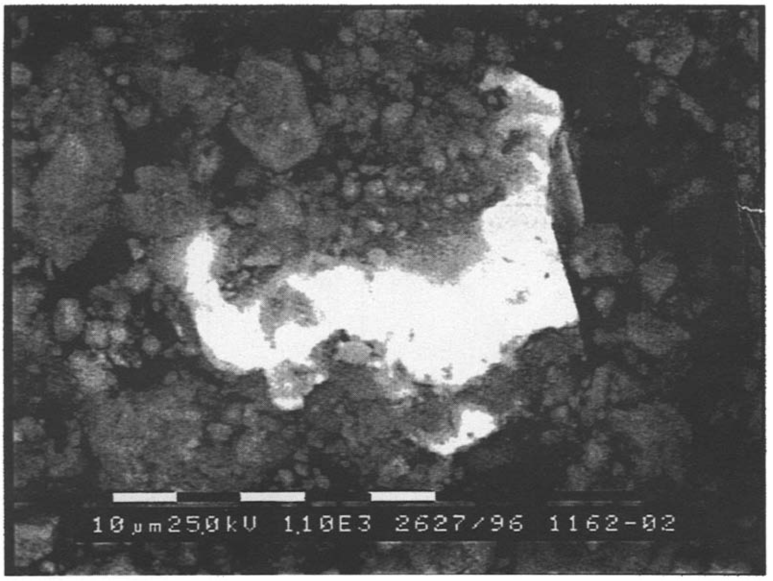

Photo 1. Particles in the phosphate rock containing Strontium and Barium

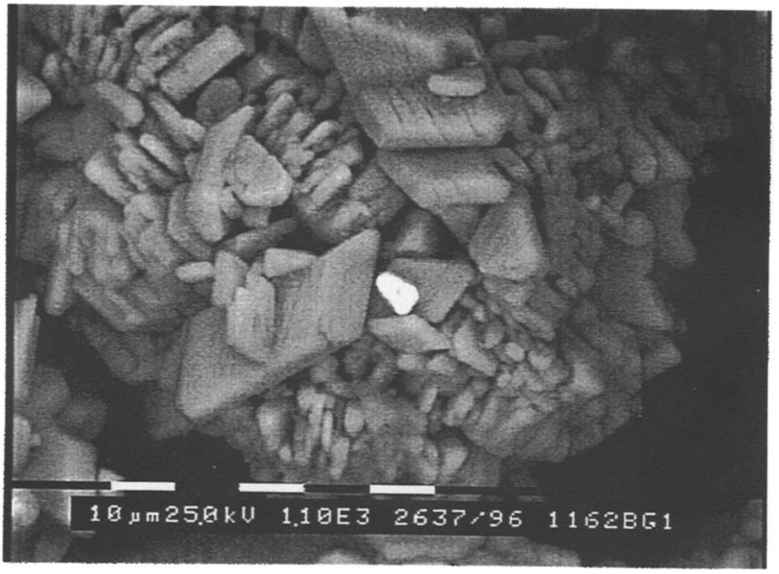

Photo 2. Particles in the phosphoric gypsum containing Sr/Ba