

THE COMPOSITION AND POTENTIAL USES OF PNOSPHOGYPSUM.

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ABSTRACT

A comprehensive analysis has been made to find out the exact composition of phosphogypsum. Results indicate a high percentage of gypsum (94.75, 1.51) which can be utilized for different purposes after removal of fluoride and phosphorus. Phosphogypsum, a by-product of the phosphate industry, therefore can be used as a raw material for the production of ammonium sulphate, sulphuric acid, plaster and expansive cement. Its evidence of low levels of heavy and poisonous metals allows its use for these purposes. It can also be used in the manufacture of building materials on account of its reasonably high content of silica. The trace levels of alkali metals allow its use in the reclamation of saline soils.

INTRODUCTION:

Utilization of phosphogypsum (PG), a by-product of the phosphate industry, has great industrial and economic importance. Large quantities are currently dumped beside the Phosphate Factory at Al-Quaim, Iraq(1) .

Their continued accumulation creates environmental hazards :Polluting ground water(2) and providing a source of windblown dust. Various workers have reported on attempts to utilize this waste material in different countries, e.g. in agriculture(3,4) ,industry(5,6), and construction(7) .

It is important to remove the harmful impurities in PG, reduce them to tolerable levels or convert them into inactive forms(8) . For this reason, precise information about the composition of PG is essential. The present study aims to elucidate this point, which should help the users of PG in industry, agriculture or construction work.

Experimental: Preparation of sample

SOLUTIONS:

1.Extraction by double deionised water:

Between 0.5 and 1.5g of PG was dissolved in cold double deionised water and heated to boiling for 15min with continuous stirring, cooled and filtered.

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The precipitate was washed several times with double deionised water and the filtrate was completed to 100 ml with double deionized water and transferred to polyethene bottles.

2. extraction with hcl (1 : 1):

An accurately weighed amount of PG (0.5-1.5 g) was dissolved in 5ml HCl(1:1). The mixture was digested for 10-15min and then cooled and filtered. The filtrate was completed to 100ml with double deionized water in volumetric flask and transferred to polyethene bottles.

3. Extraction with 2MHClO₄:

PG sample (ranged from 0.5 to 1.5g) was digested in 50ml of 2MHClO₄ for 20-30 min with continuous stirring. The suspension was cooled, filtered and completed to 100 ml with double deionized water and transferred promptly to polyethene bottles.

4.Fusion with NaOH:

A weighed sample (ranged from 0.5 to 1.5g) was transferred to a platinum crucible, and 6ml of NaOH solution (67 g/100ml) were added, mixed very well and dried at 250°C in an oven . The crucible was then transferred to a muffle furnace and the contents fused at 600°C for 30 min. The fused product was dissolved in distilled water, filtered and treated with 6ml of conc. HCl.

The solution was partially neutralised with 5MNaOH (10-15ml) added dropwise, and employing a glass electrode and pH meter. Finally, the solution was completed to 100ml with double deionized water and kept in polyethene bottles.

5.Fusion with Na₂CO₃ and ZnO:

A known weight of PG (ranged from 0.5 to 1.5g) was well mixed with 0.1g of Na₂CO₃ . and 0.5g of ZnO in platinum crucible and fused at 900°C in a muffle furnace for 30min . The fused mixture was dissolved in distilled water, filtered and neutralised with HCl (1:1) (about 1ml) to remove CO₂, and then completed to 100 ml with double deionized water The solution was stored in polyethene bottles.

Determination of moisture, combined water, silica, volatile species, mixed oxides, lime and magnesia:

The gravimetric method mentioned by Furman(7) was followed for determination of moisture, combined water , silica and insoluble matter, volatile species, mixed oxides, lime, magnesia and sulphur trioxide in PG. Moisture in PG was expelled by heating a known weight (0.5-1.5g) in an oven at 45°C. The combined water was determined by raising the temperature of these samples to 225 °C in the same oven.

Determination of some alkali metals:

Lithium, potassium and sodium were determined by flame emission photometry using Gallenkamp flame analyzer according to the procedure of Goltzman(10) On each run, the instrument was calibrated with a series of standards in the range of 0.5-30ppm. Necessary dilutions were made whenever needed.

Determination of some non- alkali metals:

Traces of heavy and poisonous metals in PG were determined by flame atomic absorption spectrometry. All measurements were carried out on model 2900Pye Unicam atomic absorption spectrometer, with an appropriate hollow cathode lamp(11). The apparatus was calibrated for each run with a series of standard solutions in the range of 0-10 ppm with necessary dilutions of the original samples.

Air-acetylene combination flame was applied with constant pressure and flow rate according to the instructions manual of the instrument (Pye Unicam) . The cold-vapour method(12,13) was employed for determination of Hg and Se.

Determination of fluoride and phosphorus:

Direct and standard addition potentiometric methods were followed for fluoride monitoring in PG using fluoride ion- selective electrode (Orion. model 94-

09) following descriptions specified in the instruction manual(14). Potential measurements were carried out using Digital pH/mV meter model 701A from Orion Research Inc. Spectrophotometric procedure of Murphy and Riley(15) with the acid and molybdate concentrations given by Stephens(16) as modified by Strickland and Parsons(17) have been exploited for phosphorus determination as phosphate .

Absorbance was measured in a 1cm cell using SAFAS 310D Model Spectrophotometer at wavelength of 882nm.

pH and specific conductivity measurements:

These measurements were made on a 1:50 PG:water suspension. pH measurements and adjustments were carried out by a Digital pH/mV meter model 701A from Orion Research Inc with a precision of ± 0.05 pH unit.

The pH-meter was calibrated before any pH-measurement with buffer solutions of 4 and 9.

Specific conductivity was measured using Radiometer conductivity meter type CDM3. Measuring accuracy is $\pm 0.6\%$ of f.s.d. + 0.002 μ S/cm, with cell constant of 1.0. Conductivities (corrected to 25 $^{\circ}$ C) were read, directly in ms / cm .

RESULTS AND DISCUSSION

Tables 1-3 depict the physical properties and chemical constituents of PG. Table 1 shows a high percentage of gypsum (94.75 _ 1.51). This table shows that PG has acidic properties possibly due to soluble acidic impurities including H_3PO_4 , H_2SiF_6 , HF and H_2SO_4 .

The major components of PG are given in Table2. The data are comparable to those obtained by Rashid et.al.(18) and by Al-Jabbari et.al.(19). Table3 displays traces of strontium, iron, nickel, cadmium, lead and zinc in PG.

Other metals like uranium, vanadium, selenium, manganese and mercury are undetectable. It could be pointed out that Iraqi PG is clean of heavy and poisonous metals and could be safely used in agriculture and construction.

Undesirable percentages of fluoride (1.03 _ 0.32) and P_2O_5 (0.59 _ 0.26) were found in PG (20)(Table2). Some measures should, however, be taken to reduce fluoride and P_2O_5 contents to the tolerable levels.

Fluorides in relatively high concentrations may act as a catalyst poison for the contact mass of SO_2 / SO_3 conversion.

Due to PG low alkali content (Table1), there is no corrosion cracking of the concrete (8).

Extraction by acids is advantageous but requires two replicates while fusion with KOH and $Na_2CO_3 + ZnO$ gives complete extraction of PG contents (Tables 1 and 2) and complete removal of phosphorus (20).

Utilisation of PG in construction requires neutral and basic media since acidic media cause corrosion and damage to the buildings, building materials and equipment used in construction. In practice, the pH of PG is raised by washing with water and adding calcium hydroxide. PG is then burnt, followed by adding of some accelerators to improve setting time and compressive strength of the Juss produced (21).

Alkali metals do not alter the properties of cement because of the similarity of properties of the compounds formed in them and those of similar compounds that do not contain them (22). However, it was mentioned that high levels of alkali metals cause efflorescence and deformity of the cement (23).

High percentages of CaO , SO_3 and silica (Table2) persuade many investigators to exploit PG as a constituent of the expansive cement. Al-Jabbari et.al.(19) found that PG should be added in 35% by weight to the ordinary Portland cement to produce the expansive cement. They deduced from their experimental investigation that the properties of the

expansive cement follow the ASTM requirements when 5% of expansive agents are added. The quality of cement Produced is competitive to that obtained in the Building Research Centre, Baghdad (24).

High percentage of CaO (Table2) or gypsum (Table1) have enabled many people to exploit PG in agriculture fields. It is used as a soluble calcium source for increasing urea efficiency in calcareous soils to control ammonia losses .

Treatments of soil with PG received higher nitrogen in plant and soil and produced higher grain yield (18) . PG can be used as a stabilizer to fix nitrogen in some fertilizers. PG with very low levels of alkali metals has enabled agriculture experts to use it as a leaching agent in the reclamation of saline soils. PG increases leaching efficiency especially with increasing soil depths, and this can be ascribed to its moderate porosity and permibility and higher dissolution rate compared to that of indigenous soil lime(25) . Its acidic properties are probably responsible for the higher efficiency of salt removal(4,26). Finally, utilisation of PG in agriculture requires dewatering of hydrated gypsum. PG is used for production of ammonium sulphate in process called the Mlerseberg process which has been extensively used in India(27) . PG is also used as a sulphur and sulphuric acid source(8) . Some countries such as Japan(6) have developed extensive efforts for PG usage. All gypsum is

supplied from the by-product phosphogypsum from fertilizer and chemical processes, especially Nissan Wet Phosphoric acid process which is currently supplying almost 50% of PG. This PG is characterised by its high quality, being suitable for the manufacture of gypsum board, cement retarder and plaster. It contains high levels of SO₃ , (>40%) low levels of water soluble P₂O₅ (<0.1%) and moisture (<10%) and has suitable crystal size which enhances setting time, decreases the initial strength of concrete and prevents cake handling troubles.

Conclusions:

1. The paper presents a comprehensive analysis of five samples of PG taken from different sites of a PG stack.
2. The results show reasonable precision of the methods employed in the analysis and reasonable accuracy when compared to values in the literature.
3. Large-scale production of PG as a by-product encourage its exploitation in construction and agriculture after removal of harmful impurities.
4. The analysis indicates that PG is almost free of heavy and poisonous metals; thus it can be safely employed in useful and profitable projects.

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Table 1 pH, specific conductivity, gypsum and alkaline metal content of PG

	1.	2.	3.	4.	5.	Average
Sample No.	1.	2.	3.	4.	5.	
pH ⁺	3.50	3.05	3.32	3.20	3.05	3.22
Specific ⁺ Conductivity ms/cm	0.0155	0.0145	0.0172	0.0145	0.0164	0.0156
Gypsum* (%)	94.46	96.64	94.58	92.21	95.87	94.75 - 1.51
Li ₂ O (%)	0.014	0.021	0.015	0.014	0.022	0.017
K ₂ O (%)	6.39 × 10 ⁻³	5.62 × 10 ⁻³	9.12 × 10 ⁻³	3.15 × 10 ⁻³	6.71 × 10 ⁻³	6.20 × 10 ⁻³
Na ₂ O (%)	0.033	0.046	0.032	0.034	0.047	0.038

+ 1g of physphogypsun shaken with 50 ml of double deionized water .

* as CaSO₄ . 2H₂O

Each value in the table is an average of five measurements for each sample. Average coefficient of variation (c.v.) in each case is within the range of 1.45 – 3.45% . Correlation coefficient of the linear ranges is 0.995.

Table 2.. Major chemical components of physphogypsun (in percentages)

	1.	2.	3.	4.	5.	Average
Sample No.	1.	2.	3.	4.	5.	
Moisture	0.48	0.09	0.17	0.18	0.34	0.25
Combined water	19.49	19.36	19.79	20.19	19.57	19.68
Loss by (a) ington	2.02	2.10	1.68	1.58	1.79	1.83
Silica (b)	2.30	1.18	1.36	1.85	1.86	1.84
Mixed (c) oxides	1.98	2.11	1.72	1.29	2.21	1.86
CaO	30.55	29.56	28.91	30.22	29.96	29.84
MgO	0.09	0.12	0.14	0.19	0.08	0.12
SO ₃	45.20	44.18	44.58	42.60	43.58	44.03
F (d)	0.86	0.66	1.32	1.60	0.88	1.03
Total	102.79	99.99	99.67	99.70	100.27	100.48

- (a) May include CO₂ , Cl₂ and organic material .
- (b) Silica and insoluble matter .
- (c) Al₂O₃, Fe₂O₃ and P₂O₅ .
- (d) After Al-Hitti *et.al.*(20) .

Each value is an average of five measurements for each sample.

Average coefficient of variation (c.v.) in each case is in the range of 1.40 – 6.55% .

Table3.. physhogypsum contents of metals in ppm.

Sample No.	Sr	Co	Ni	Fe	Cd	Pb	Zn
1.	320	250	45	200	3.2	52	5.3
2.	400	150	43	170	4.3	47	4.8
3.	410	130	46	160	3.5	42	4.3
4.	360	180	47	220	3.8	41	4.6
5.	420	130	43	220	4.6	43	4.9
Average	382	168	44.8	194	3.9	45	4.8

Each value is an average of five measurements for each sample .

Correlation coefficient of the linear ranges is 0.992.

Average coefficient of variation (c.v.) in each case is in the range of 1.06 – 4.56% .

التركيب والاستعمالات الواسعة للفوسفوجبسوم

د. اسماعيل خليل الهيتي

الخلاصة :

اجري تحليل شامل للفوسفوجبسوم لمعرفة محتواه الدقيق . وقد اوضحت النتائج النسبة العالية للجبس في الفوسفوجبسوم (1.51 _ 94.75) ،والذي يمكن استغلاله لأغراض مختلفة بعد إزالة أو خفض نسبي الفلوريد والفسفور إلى المستويات المقبولة . ولهذا أمكن استثمار هذا الناتج العرضي لصناعة الفوسفات كمادة خام لإنتاج كبريتات الأمونيوم وحامض الكبريتيك والبلاستر والسمنت القابل للتمدد . ولقد أثبت في هذا البحث المستويات الواطئة جداً للفلزات الثقيلة والسامة في الفوسفوجبسوم بما يعزز استعماله في الأغراض أعلاه . ويمكن أن يستعمل أيضاً في صناعة مواد البناء بسبب احتوائه على نسبة عالية ومعقولة من السيليكا ، كما أن وجود آثار قليلة جداً من الفلزات القلوية في الفوسفوجبسوم قد أهلت استعماله في إصلاح الترب الملحية .