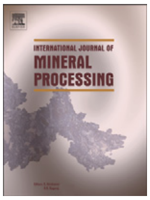
International Journal of Mineral Processing 123 (2013) 87–93

Contents lists available at ScienceDirect

International Journal of Mineral Processing

journal homepage: www.elsevier.com/locate/ijminpro



Solubility study and valorization of phosphogypsum salt solution☆

Ines Hammas *, Karima Horchani-Naifer, Mokhtar Férid

Laboratory of Physical Chemistry of Mineral Materials and their Applications, National Research Center in Materials Sciences, Technopole Borj Cedria B.P. 73- 8027 Soliman, Tunisia

ARTICLE INFO

Article history:
Received 8 March 2013
Accepted 26 May 2013
Available online 2 June 2013

Keywords:
Calcium carbonate
Hydrated sodium hydrogenosulfate
Phosphogypsum solubility
Sodium chloride aqueous solution
Valorization

ABSTRACT

This paper aims to transform a phosphogypsum (PG) solution to non-toxic and industrially useable compounds. For that, the solubility of the Tunisian PG was studied in different aqueous solutions in order to determine which of them is best for its dissolution. After monitoring the ionic conductivity of each solution as a function of the added amount of PG, it was concluded that the latter is better dissolved in a sodium chloride solution. A maximum value (5.3 g/L) was obtained in 25 g/L NaCl solution. The analysis of the filtrate, obtained after PG dissolution, had shown that it mainly contains sodium, sulfate and calcium ions. The suggested valorization method comprises formation of calcium carbonate after $(NH_4)_2CO_3$ addition to the filtrate's solution, decarbonation with H_2SO_4 and evaporation of the final solution. The formed $NaHSO_4.H_2O$ crystals were washed with acetone and dried in the air. All the compounds produced in this work were identified by infrared spectroscopy and X-ray diffraction.

1. Introduction

Phosphogypsum (PG) is an acidic by product of the phosphate fertilizer industry, formed during the production of phosphoric acid from phosphate rock. It is composed mainly of gypsum ($CaSO_4.2H_2O$) but contains various harmful impurities which depend on the type of the attacked phosphate rock (magmatic or sedimentary), the used process (dihydrate, hemihydrate and recrystallization) and the storage duration (which affects the amount of soluble impurities in water). Up to now, large amounts of PG have been produced worldwide and it is estimated that if historic trends continue, production will increase to several hundred million metric tons annually. In Tunisia, the production rate exceeds 10 million tons per year. The problems of pollution generated by this by product have been discussed by many authors in the world. For many years, the "Groupe Chimique Tunisien" and the Tunisian Environmental Ministry are dealing with the problems of its management and valorization (Sfar Felfoul et al., 2002).

However, because of economic restraints (e.g. land price) and pressing environmental issues, the development of a safe disposal procedure is necessary. Although, the best option for dealing with the PG problem appears to be the commercial use of this material in the agriculture (e.g. amelioration of acid soils) and construction industry (building/road construction), only a relative small portion of the PG produced (14%) is reprocessed, a significant part is dumped into water bodies (28%) and the largest amount of the material is accumulated in large sludge ponds and retaining stockpiles (Papanicolaou et al., 2009).

The extraction of value-added elements from PG has been the subject of several works. Such processes require generally a concentration step especially in the case of trace elements extraction. Among these steps include PG dissolution in water (see invention US 0419318A1) which produces in some procedures about 20 L of waste solution after dissolving only 100 g of PG. Until now, no method describing the valorization of this solution to valuable compounds has yet been published. Such concentration step requires firstly the determination of the ideal solution allowing a better dissolution of the solid waste and keeping the elements in question intact. Previous researches have studied the solubility of gypsum in the presence or not of electrolyte in the solution (Papanicolaou et al., 2009; Pouget, 1968; Oster and Frenkel, 1980). Results have shown that gypsum solubility is enhanced in salt solutions.

In the present work, we studied the solubility of Tunisian PG in different aqueous solutions and chose the one giving the highest value of solubility for the rest of the study. Then, a method was proposed in order to benefit from the obtained filtrate and transform it into useful products. The reaction process detailed after here, leads to the formation of calcium carbonate and hydrated sodium hydrogenosulfate rods.

Calcium carbonate is widely used in rubber, plastic, printing ink, paper making dope, toothpaste, cosmetics and food industries (Domka, 1995; Passaretti et al., 1993), for its low cost, excellent physical and chemical properties (Shen et al., 2007).

Sodium hydrogenosulfate is used in dyeing, in the manufacture of cement, paper, soap, and as an acid-type cleaner. It is a non-toxic compound which is soluble in water.

2. Materials and methods

The PG studied in this work comes from Sfax stockpiles. Its age exceeds 40 years.

☆ Foundation item: Project supported by the Ministry of Higher Education and Scientific Research of Tunisia.

* Corresponding author. Tel.: +216 7932 5250; fax: +216 7932 5314.
E-mail address: ines_hammas@yahoo.fr (I. Hammas).

0301-7516/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.minpro.2013.05.008

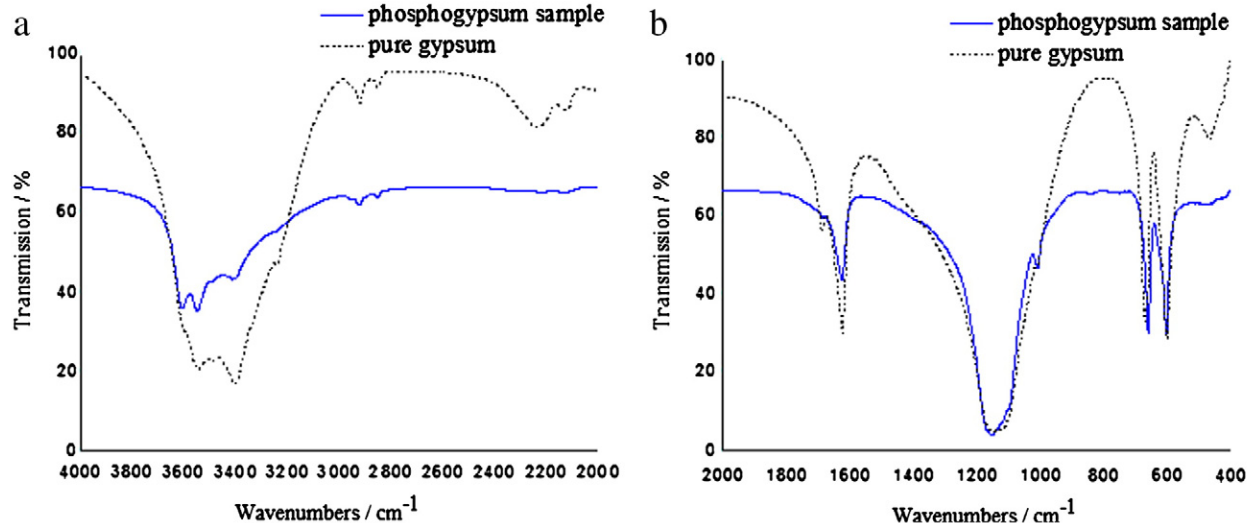


Fig. 1. Infrared spectra of the raw phosphogypsum and pure gypsum ((A): 4000 – 2000 cm^{-1} range and (B): 2000 – 400 cm^{-1} range).

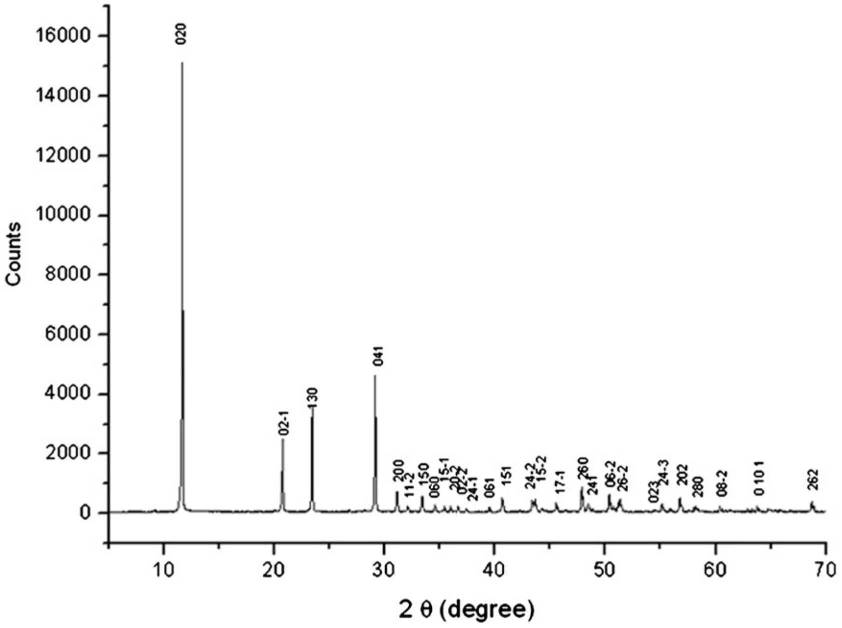


Fig. 2. X-ray diffraction pattern of the Tunisian phosphogypsum.

The X-ray powder diffraction (XRD) patterns of all samples were recorded on an X'PERT Pro PANAnalytical diffractometer with Cu Kα radiation ($\lambda = 0.15418$ nm).

Infrared spectra were performed on a FT-IR System Perkin Elmer spectrometer using KBr pellets in the region of 4000–400 cm^{-1}.

The solubility was determined by conductivity measurements of a fixed volume of water to which were added small masses of the raw sample. The measurements were performed using a TACUSSEL conductivimetre (CDRV 62) at room temperature after stirring the solution for 2 min. The change in the slope of the curve indicates the saturation of the solution and consequently allows solubility value determination (expressed in g/L).

3. Results and discussion

3.1. Sample characterization

The sample (PG) was firstly analyzed by infrared spectroscopy and X-ray diffraction. The superposition of the infrared spectrum of the raw PG with that of pure gypsum, displayed in Fig. 1, shows their great similarity. This is highlighted by the presence of water molecules vibrations $\nu_{O\text{-}H}$ and $\delta_{O\text{-}H}$ observed respectively at 3600-3200 cm^{-1} and 1684 – 1622 cm^{-1} as well as the presence of those of sulfate groups. The vibrational modes for the 2218 and 2135 cm^{-1} are assigned to the $\nu_{O\text{-}S\text{-}O}$ stretching modes (Bourgier, 2007). The vibration located at the 1152-1099 cm^{-1} range is attributed to the stretching modes

Table 1
Tunisian phosphogypsum composition.

Composition (%)	Sample of this work	Typical composition of phosphogypsum (Charfi, 1999)
SO_3	41.9	44
CaO	27.21	32.7
Total P_2O_5	2.46	0.65
MgO	0.066	0.1
F	0.02	1.2
Fe_2O_3	0.042	0.1
Al_2O_3	0.3	0.16