Study of physico-chemical characteristics of nickel insertion in phosphogypsum

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ABSTRACT

The main purpose of this work is study the influence of the insertion metal ions Ni (II) in the phosphogypsum produced by sulfuric acid attack of tricalcium phosphate. Indeed, the maximum content of heavy metals calcium sulfate that can absorb was determined. The added ions are ($NiCl_2$, $6H_2O$) with mass concentrations ranging from 5% to 50%. The samples prepared were characterized by various methods, such as X-ray diffraction (XRD), infrared spectroscopy and inductively coupled plasma atomic emission spectroscopy (ICP-AES). The results of this study showed that the limit of insertion of metal cations in calcium sulfate is limited to 30% for nickel.

Keywords: Phosphogypsum; Nickel; Insertion; XRD; IR ; ICP-AES

1. INTRODUCTION

The increasing worldwide interest carried to the environmental preservation, attracted much industrialists attention to find a technical means to reduce or to valorize the solid waste. Indeed, phosphate industry, particularly the production of phosphoric acid, rejects phosphogypsum which is rich in calcium sulfate and contains heavy metals such as nickel [1-3].

The environmental problems of phosphogypsum are directly related to the rock phosphate. In this context, we realized this reaction with $Ca_3(PO_4)_2$ to avoid any interaction with heavy metals in order to find the insertion capacity of these metals in phosphogypsum.

In fact, the tricalcium phosphate structure $Ca_3(PO_4)_2$ is able to accept a large number of cationic substitutes [4-7]. This can significantly change their physical and chemical properties. Indeed, the Ca^{2+} ions can be exchanged with divalent ions such as Sr^{2+}, Cd^{2+}, Ba^{2+}, Cu^{2+}, Ni^{2+} and Co^{2+}. These substitutions have been the subject of some research projects in the field of heterogeneous catalysis and wastewater treatment [8-14].

There are several analytical methods which can be used on sample characterization. To perform the determination of chemical elements usually X-ray diffraction , infrared spectroscopy and inductively coupled plasma . There are several strategies to digest solid samples, however, in some cases the decomposition does not occur in micro level, so the recovery of the total concentration of selected elements is not adequate . To overcome this difficulty it is fundamental to do experimental tests using distinct accessories and/or reagents. After the spectrometry analysis on the digested sample, the total content of the chemical element can be obtained[15].
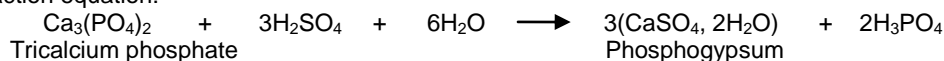
In this work is to study the physical and chemical characteristics of the insertion of nickel in the calcium sulfate in order to determine the maximum levels of these metals can be absorb by calcium sulfate. This was realized by following the insertion by the X-ray diffraction, infrared spectroscopy and atomic emission spectrometry with inductively coupled plasma (ICP-AES).
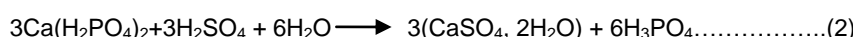
2. EXPERIMENTAL

2.1 Materials and Methods

The phosphogypsum was prepared at 80°C, and after 1 hour 30 minutes of maturation, the hot solution is filtered to recuperate the phosphoric acid. Thereafter, the solid was washed with hot bidistilled water and pure acetone. It is finally dried at 80°C.

The overall reaction equation:

$$Ca_3(PO_4)_2 + 3H_2SO_4 + 6H_2O \longrightarrow 3(CaSO_4, 2H_2O) + 2H_3PO_4$$

Tricalcium phosphate ⟶ Phosphogypsum

This reaction is carried out in two steps:

$$Ca_3(PO_4)_2 + 4H_3PO_4 \longrightarrow 3Ca(H_2PO_4)_2 \quad \ldots\ldots\ldots\ldots\ldots \quad (1)$$

$$3Ca(H_2PO_4)_2 + 3H_2SO_4 + 6H_2O \longrightarrow 3(CaSO_4, 2H_2O) + 6H_3PO_4 \ldots\ldots\ldots\ldots(2)$$

The same reaction is performed by adding the cations Ni (II) with mass concentrations ranging from 5% to 50% according to the following reactions:

$$Ca_3(PO_4)_2 + xNi^{2+} \longrightarrow Ca_{3-x}Ni_x(PO_4)_2 + xCa^{2+}\ldots\ldots\ldots\ldots\ldots\ldots(3)$$
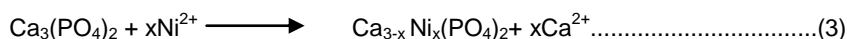
The fixation mechanism is described as the insertion of the metal on the surface of tricalcium phosphate, followed by substitution with cationic calcium [16]. The metal introduction takes place in the second reaction (2)

3. RESULTS AND DISCUSSION

3.1 Analysis of ionic groups by infrared spectroscopy in the case of nickel

The results of the IR spectroscopy analysis of calcium sulfate prepared in the presence of nickel contents ranging from 5% to 50% are shown in the following figure 1.
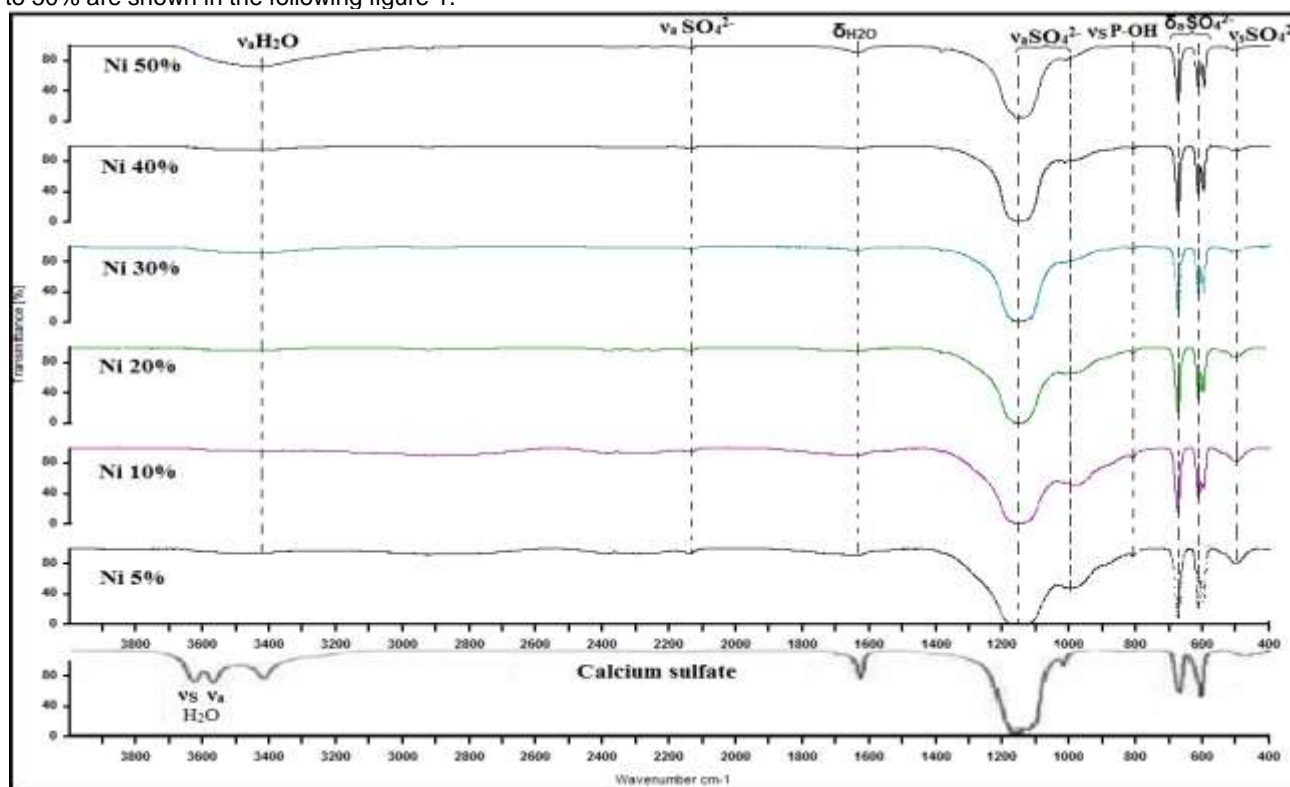
Fig 1: Infrared absorption spectra of solid samples in the presence of nickel

Analysis of these infrared absorption spectra allowed the characterization of products formed in phosphoric medium. Band positions are shown in Table 1.

Table1. Assignment of characteristic bands of different obtained solids

$Ca_{1-x}-Ni_x-SO_4, 2H_2O$	characteristic bands	spectral range (cm^{-1})	Phase concerned
x=0	$\delta_a SO_4$	680 et 600	$CaSO_4, 0.5H_2O$
	$v_a SO_4$	2132 et 1153	$CaSO_4, 2H_2O$
	δH_2O	1620	
	$v_s HPO_4$	850	$CaHPO_4, 2H_2O$
	$v_a HPO_4$	980	
	$v_s H_2O$	3406	
	$v_a H_2O$	3620 et 3550	
5%≤x≤50%	$v_s SO_4$	525-512	$CaSO_4, 2H_2O$
	$\delta_a SO_4$	673 et 612	$NiSO_4$
	$v_a SO_4$	2134 et 1154	
	δH_2O	1630	
	$v_s HPO_4$	808	$CaHPO_4,2H_2O$
	$v_a HPO_4$	1012	
	$v_s H_2O$	3410	

I S S N   2 3 2 1 - 8 0 7 X
V o l u m e   1 2   N u m b e r 6
J o u r n a l   o f   A d v a n c e s   i n   C h e m i s t r y

	$v_a H_2O$	3530	

Infrared absorption spectra of the different solid samples are recorded in the area ranging from 4000 to 400 cm^{-1} in a percentage range of transmission equal to 40. Figure 2 shows a comparison of infrared spectra of solid solutions obtained with calcium sulfate. The observed bands at 808 cm^{-1} is probably due to the vibrations of HPO_4^{2-} which absorb in the same region. The intensity of this band varies with the rate of nickel incorporated into the calcium sulfate crystal.

From the quantities of nickel less than 30%, the spectra have the same shape as that of calcium sulfate, with a slight shift of some vibration bands. This discrepancy is probably due to the existence of exchange reactions between Ca(II) and Ni(II). Over 30% of Ni, we notice the disappearance of the bands of the P-O binding. This explains why the insertion of nickel is stopped. The observed band at 3406 cm^{-1} is usually attributed to symmetric stretching vibrations of OH$^-$ ions. This suggests that the introductions of Ni(II) ions significantly alters the intensity of this band and of that corresponding to the OH groups and the Ni ions are exchanged as ($NiSO_4$) .

3.2 Quantitative phase analysis by XRD in the case of nickel

The obtained X-ray diffraction patterns of the series of solid samples prepared in the presence of varying nickel contents from 0 to 50% are shown in figure 2.
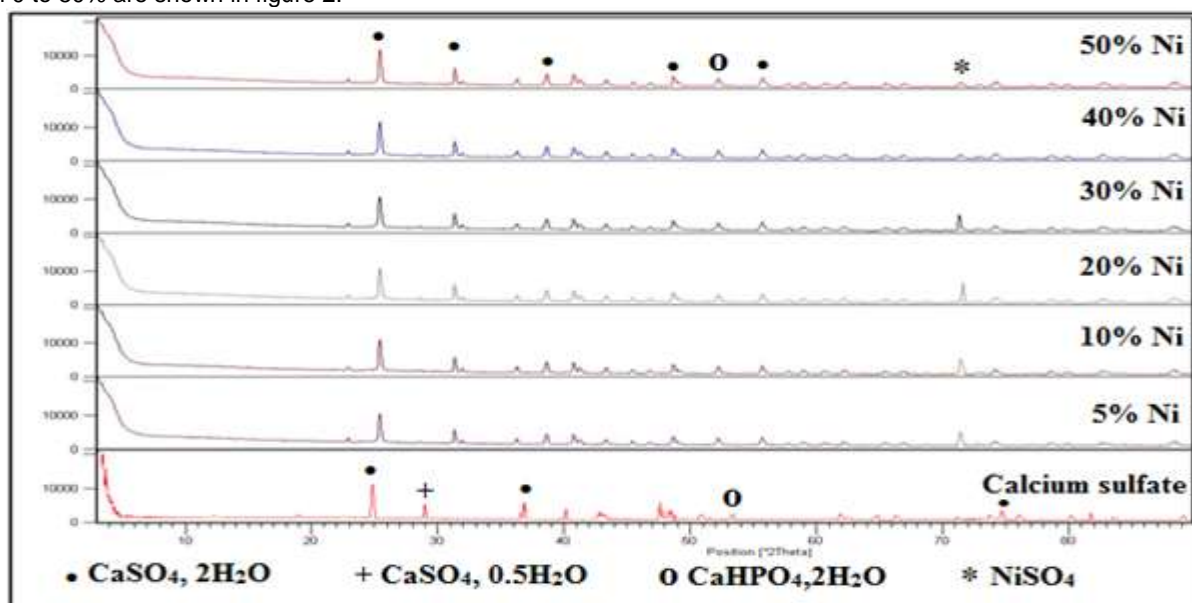

Fig 2: Diffraction patterns of X-rays of calcium sulfate prepared with varying nickel contents

The X-ray diffraction patterns (figure 2) reveal the presence of ($CaSO_4$, $2H_2O$), ($CaSO_4$, $0.5H_2O$), ($CaHPO_4$, $2H_2O$), and ($NiSO_4$) phases. A perfect similarity is observed between these diffraction patterns of X-rays (5% to 50% mass percentage of nickel) with a small displacement of the peaks. From a concentration of 5%, there is the appearance of the peak characteristic of the presence of nickel sulfate ($NiSO_4$) (2θ =72). The intensity of this peak increases with progressive addition of nickel.

In Figure 2, we note that when the nickel content reached a maximum of 30%, the peak intensity decreases.

3.3 Analysis by inductively coupled plasma atomic emission spectrometry of phosphoric acid

To test the insertion system, the following parameters were used: insertion efficiency of the system (percentage of nickel (II) biosorption) indicating the percentage of exchanging metal ions relative to the initial amount C_i, and insertion capacity C_f. The percentage of nickel (II) biosorption was calculated by using Equation 1.

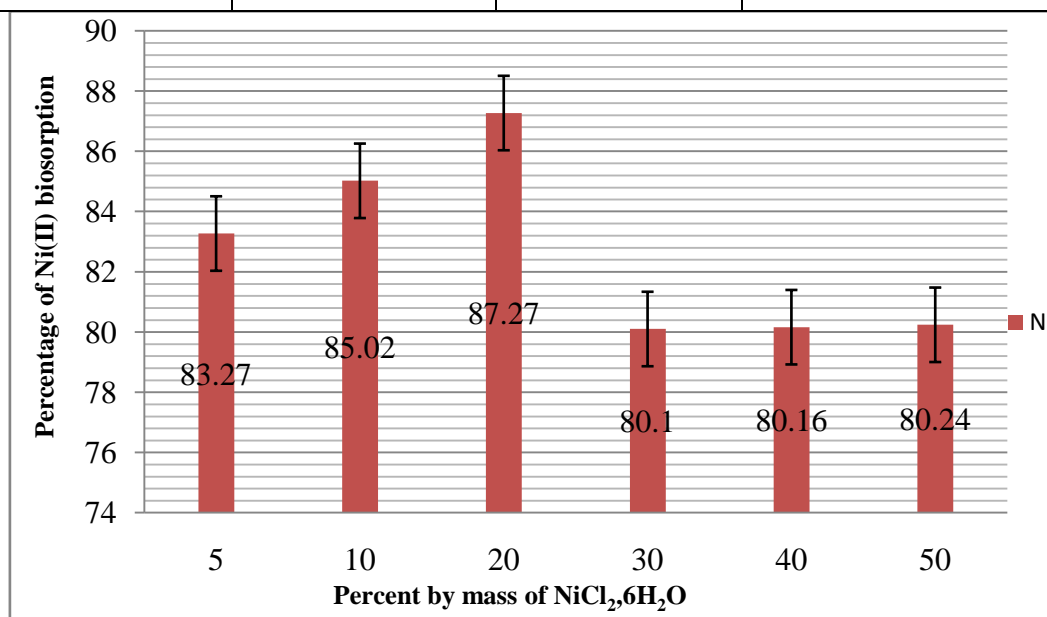$$percentage\ of\ nickel(II)\ \text{biosorption} = \frac{(C_i - C_f)}{C_i} * 100\% \quad (Equation\ 1)$$

where C_i = initial nickel (II) concentration (%), C_f = final concentration of nickel (II) concentration (%)

This result is confirmed by chemical analysis of phosphoric acid solutions by analyzing the residual amount. The amounts are summarized in the following table:

Table2. Results of chemical analysis of phosphoric acid containing different contents of nickel (%Mass: percent by mass)

%Mass. NiCl$_2$, 6H$_2$O	%Mass. C$_i$ (Ni(II))	%Mass. C$_f$ (Ni(II))	Percentage of Ni (II) biosorption
5	1.220	0.204	83.27
10	2.450	0.367	85.02
20	4.910	0.625	87.27
30	7.372	1.467	80.10
40	9.830	1.950	80.16
50	12.280	2.426	80.24

Fig 3: Percentage of changes as a function of percent by mass

From these results, it is obvious that the nickel ions content increases in the recovered acid, when this content is increased in the reactor solution from 5% to 50%, this content does not exceed the limit in the calcium sulfate which is of the order of 30% (% Rem=80%).

CONCLUSION

In this work, we were interested in the exchange of the ions Ca^{2+} by nickel in the calcium sulfate. The results of infrared absorption spectroscopy and the X-ray diffraction of the all solids show that the calcium ion exchange with nickel in the tricalcium phosphate leads to a modification on the characteristics of calcium sulfate with a displacement and enlargement of some bands of vibration. All chemical analysis results show that the content of nickel and ions increases regularly in the produced acid, when the content of reactant solutions increases. Also, these results explain clearly the presence of the phases (NiSO$_4$), and show that the insertion of the metal cations obtained in calcium sulfate is limited at 30 % of the nickel. The results of this study explain that the calcium sulfate prepared characteristics are favourable for removal metal cations Ni(II) from the aqueous solution and wastewater.

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