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Ternary phase diagrams of $CdSO_4$–$NiSO_4$–H_2O at 40 °C and 80 °C

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ABSTRACT

The separation of cadmium and nickel from sulfate leach liquors of waste Ni–Cd batteries is investigated by using ternary phase diagrams. Experimental studies are carried out to obtain ternary phase diagrams of nickel sulfate, cadmium sulfate and water mixture at 40 °C and 80 °C. The eutectic point is determined to be composed of $CdSO_4.8/3H_2O + NiSO_4.6H_2O$ and $CdSO_4.H_2O + NiSO_4.6H_2O$, for 40 °C and 80 °C, respectively, while two univariant curves and two crystallization regions are observed corresponding to $CdSO_4.8/3H_2O$ and $NiSO_4.6H_2O$ at 40 °C, $CdSO_4.H_2O$ and $NiSO_4.6H_2O$ at 80 °C. Both low (40 °C) and high (80 °C) temperature systems belong to a simple saturated type while no double salts or solid solutions exist.

1. Introduction

Today, handling of waste batteries is gaining more importance due to increasing economical and environmental concerns. In order to keep sustainability in battery consumption, recycling seems to be the favored handling option. Recycling methods for waste batteries can follow either pyrometallurgical or hydrometallurgical routes [1].

Pyrometallurgical processes use heat to selectively volatilize metals at high temperatures. These processes are simple and do not require crushing of batteries to fine pieces. However, they are energy-intensive and produce a substantial amount of emissions [2]. Although the utilization of pyrometallurgical processes has decreased today, there are still plants in operation, some of which are BATREC (Switzerland), SNAM (France), Sab Nife (Sweden), Inmetco (USA) and Fernwarme (Austria) [2,3].

Hydrometallurgy, on the other hand, benefits from aqueous chemistry rather than heat for the recovery of metals. Leaching is the basic hydrometallurgical process and it is followed by several chemical processes like solvent extraction, electrowinnig, crystallization, precipitation, etc. Compared to pyrometallurgical processes, hydrometallurgical processes are more economical, effective, predictable, controllable and eco-friendly [2,4,5].

Crystallization is one of the most used separation techniques in hydrometallurgical processes. Phase diagrams provide a basis for crystallization [6–11]. In the case of recycling of Ni–Cd batteries via crystallization, ternary phase diagram of $CdSO_4$–$NiSO_4$–H_2O system is crucial. However, such a phase diagram has not been reported in the literature.

The aim of this study is to investigate the possibility of selectively crystallizing cadmium sulfate and nickel sulfate from leach liquors of spent Ni–Cd batteries. Experimental studies are carried out in order to obtain ternary phase diagrams of nickel sulfate, cadmium sulfate and water mixture at 40 °C and 80 °C.

2. Experimental

2.1. Reagents

The chemicals used are of analytical grade and were obtained from Sigma-Aldrich Inc. and Merck Chemicals ($CdSO_4.8/3H_2O$, purity 99% and $NiSO_4.6H_2O$, purity 99%). No additional purification was made for the chemicals (Table 1). ASTM Type I ultra-pure water (18.2 MΩ.m resistivity) is used in experiments and analyses.

2.2. Analysis

Nickel and cadmium concentrations of solutions are determined by inductively coupled plasma optical emission spectroscopy (ICP-OES, Thermo Scientific 6000 series).

Crystallographic structures of wet solid residues are determined by X-ray diffraction (XRD, Rigaku Miniflex 600) analysis and confirmed by Schreinemakers' method of wet residues.

According to this method, points representing the compositions of synthetically prepared initial solution, wet-solid phase and saturated solution in a ternary diagram must be on the same line and

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Table 1
The sample provenance table for all chemicals.

Chemical name	Source	Purity (% by mass)	Purification method	Analysis methods
$CdSO_4.8/3H_2O$	Sigma-Aldrich Inc.	>99.0	None	ICP
$NiSO_4.6H_2O$	Merck Chemicals	>99.0	None	ICP

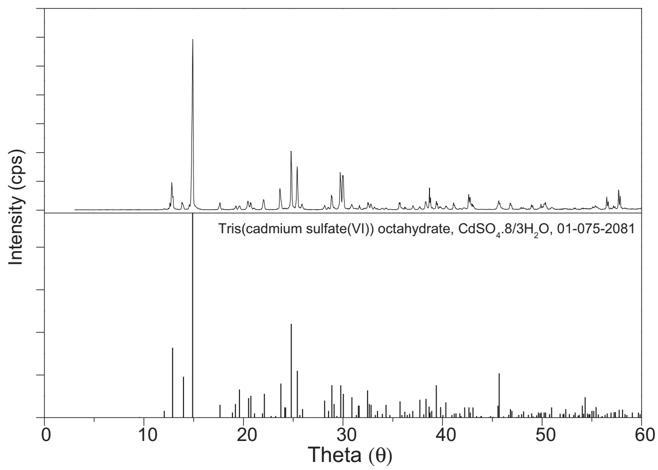

Fig. 1. XRD patterns obtained for experimental $CdSO_4.3/8H_2O$ and reference JCPDS file (075-2081).

the line passed through these points is used to find the solid phase composition at equilibrium. All samples of different solutions must be in equilibrium with the same solid phase. The hydration state of the solid phase is also determined graphically [11,12].

2.3. Experimental procedure

The starting solutions of $NiSO_4$–$CdSO_4$–H_2O system at various concentrations are prepared with an excess amount of the solids ($CdSO_4.8/3H_2O$, $NiSO_4.6H_2O$) and placed in 100 ml screw-thread bottles. The bottles are then agitated in a shaking water bath (Julabo SW22), which is set to the desired temperature. The variation in the temperature is less than ±0.1 °C. Ternary phase diagrams of $NiSO_4$–$CdSO_4$–H_2O are generated at temperatures of 40 °C and 80 °C. For each temperature, 18 mixtures at various concentrations

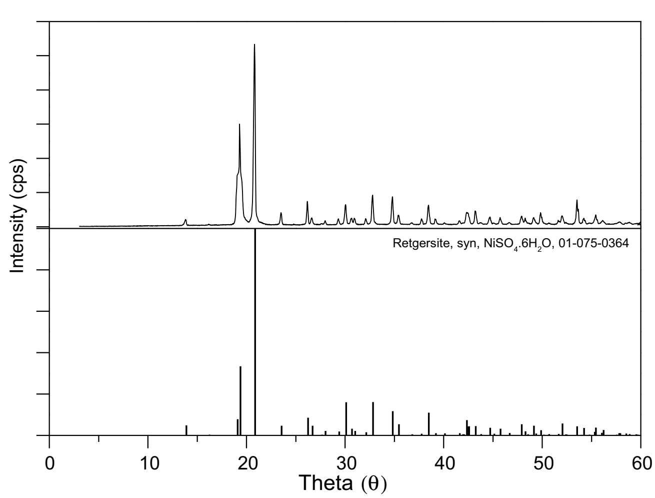

Fig. 2. XRD patterns obtained for experimental $NiSO_4.6H_2O$ and reference JCPDS file (075-0364).

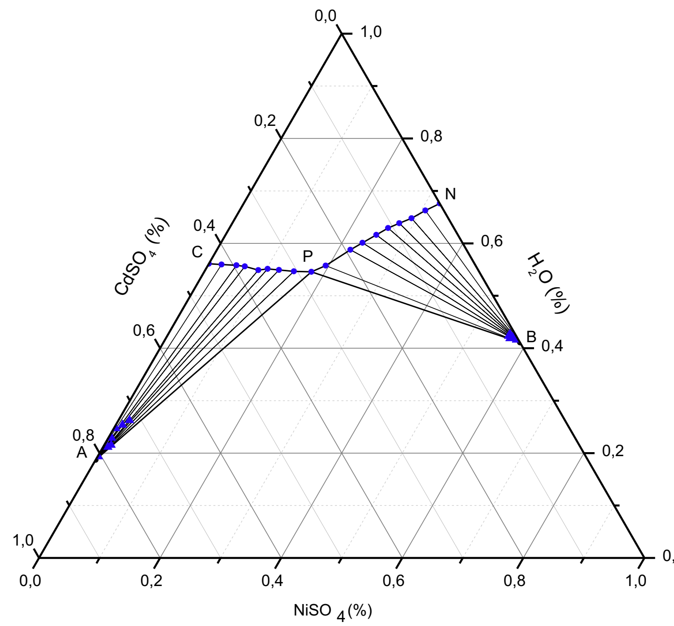

Fig. 3. Ternary diagram of $CdSO_4$–$NiSO_4$–H_2O at 40 °C.

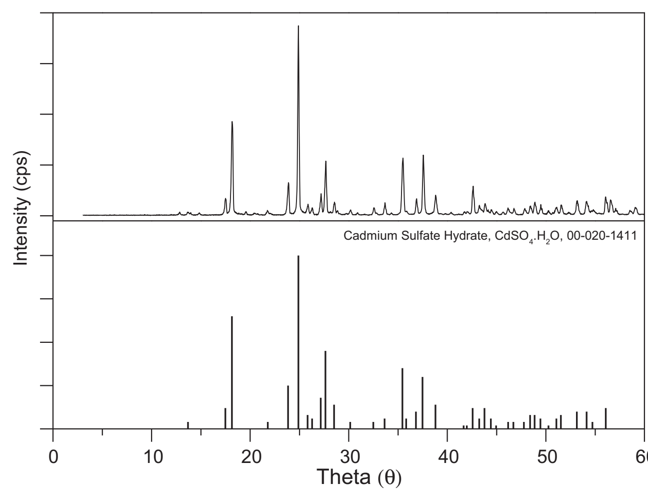

Fig. 4. XRD patterns obtained for experimental $CdSO_4.H_2O$ and reference JCPDS file (020-1411).

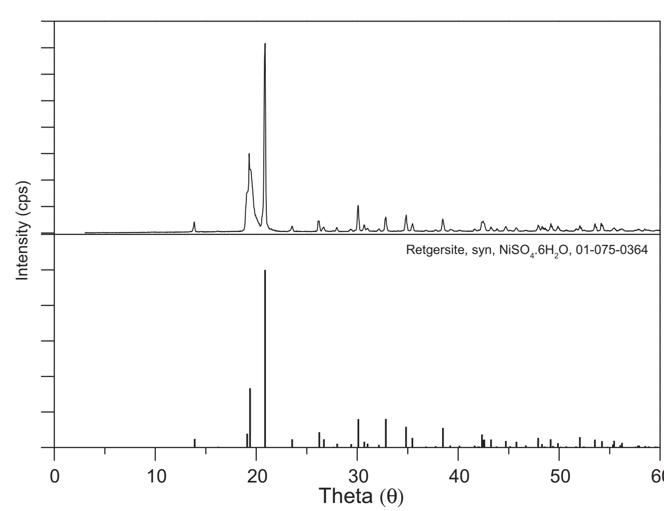

Fig. 5. XRD patterns obtained for experimental $NiSO_4.6H_2O$ and reference JCPDS file (075-0364).