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Purification of Nickel Sulfate by Batch Cooling Crystallization

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Abstract

Cooling crystallization was successfully carried out in a batch cooling crystallizer from impure acidic solutions to recover nickel as nickel sulfate salt with three different cooling rates. The compositions of the solutions included impurities of sodium, magnesium, chloride and sulfuric acid in order to mimic industrial nickel electrowinning process solutions. The results show that nickel sulfate hexahydrate (NiSO₄·6H₂O) mainly crystallized and its solubility and purity decreased with the increase in the mass ratio of chloride to sulfate. Cooling rates did not have significant influence of crystal purity, it did however, affect the filter cake moisture; lower moisture can be obtained with lower cooling rate. The sequence of impurity removal efficiency from high to low was Cl, Na and Mg.

Keywords: Batch cooling crystallization, Impurity, Nickel sulfate, Purification

1. Introduction

Globally, serious problems including climate change, diminishing natural resources and increased urbanization require that humanity creates a successful, sustainable carbon-neutral circular economy in order to maximize the use of materials and maintain their useful value as long as possible. Consequently, the dramatic growth in demand for green energy such as electronic vehicles and accumulators stems from recent rapid social developments and the need to protect the environment. Bloomberg New Energy Finance estimates that electric vehicles will account for 54 % of vehicles sales globally by 2040 [1]. Understandably, along with high levels of battery manufacture there is also significant amounts of associated battery wastes. Moreover, various valuable metal elements such as lithium, nickel, cobalt and copper are contained in these waste streams [2, 3]. As one of the most valuable metals, nickel is widely used in numerous industrial applications due to its catalytic, electronic and anticorrosion properties [4, 5]. Nickel recovery from industrial hydrometallurgical process streams, electrowinning side-streams, urban mining and other waste sources is important not only from the economical point of view, but also in terms of the future sustainability of finite resources. To date, a number of different recovery and purification methods for nickel recovery have been reported in the literature and include techniques like chemical precipitation, anti-solvent precipitation, leaching, electrowinning and hydrogen reduction.

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Furthermore, ion exchange, adsorption, membrane filtration and electrochemical treatment have been used for nickel separation [5-8].

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As one of the most efficient separation and recovery technologies, cooling crystallization can be used to recover substances whose solubility is highly dependent on temperature in order to obtain a pure product. Crystal properties such as purity and crystal size have a significant impact on downstream processing and end usage. For example, one possible nickel sulfate application is the production of battery-grade NiSO₄ that requires a typical impurity level below 100 ppm [9]. Nevertheless, currently there is limited literature data concerning the effect of impurities on the crystallization of nickel sulfate from multi-component aqueous solutions. In addition, impurities present in solution can have complex effects on the solubility of the precipitating compound in water, whereas with salting-in the presence of the third component results in a higher solubility than that in pure water. [10] Moreover, the effect of an unwanted substance in the solution strongly depends on the system, e.g. the presence of a foreign ion may either accelerate or inhibit nucleation, which subsequently influences the rate of crystal growth. Therefore, the role of impurities has to be considered, especially in industrial solutions that are invariably impure.

Generally, relatively high amounts of nickel remains in the side-streams from the electrowinning process. Sulfuric acid is commonly consumed during the leaching process, and thus sulfate ion with a high concentration is also present in these streams together with other impurities including magnesium, chloride and sodium. Moreover, the solubility of nickel sulfate is highly dependent on temperature and reduces in the presence of sulfuric acid [11]. Therefore, in the present work, the potential and feasibility to recover nickel as nickel sulfate by batch cooling crystallization from an acidic multi-component process solution was investigated. The compositions of the solutions used were formulated such that they were similar to those used in industrial electrowinning process. How to obtain the nickel sulfate crystals with high purity level, what is the role of impurities and what is the effect of acidic solutions having pH below 1 are the main research targets of this research work.

2. Materials and methods

2.1 Materials

Analytical reagent grade of chemicals, nickel sulfate heptahydrate (NiSO₄·7H₂O, purity \geq 99.0%, Honeywell), nickel chloride hexahydrate (NiCl₂·6H₂O, purity \geq 98.0% Merck), sulfuric acid (H₂SO₄, purity 95-97%, Merck), magnesium chloride hexahydrate (MgCl₂·6H₂O, purity \geq 99.0%, VWR), and sodium chloride (NaCl, Purity 99.8%, Riedel-de Haën) were used without further purification to prepare the different impure process-type solutions. Distilled water was used throughout the experimental procedure.

2.2 Experimental methods

Cooling crystallization was studied with various synthetic nickel solutions that contained impurities and the presence of sulfuric acid. Tab. 1 shows the mass ratio of the different substances within the synthetic solutions.

(Table 1)

Initially, the solubility of NiSO₄ in the impure acidic solutions were studied by visual observation. For each experiment, differing amounts of the chemicals listed in Tab. 1 were firstly prepared in a conical flask and the temperature of the solution during the solubility measurement was controlled by a thermal sensor connected to a magnetic stirrer (Hei-connect, Heidolph). When the chemicals added initially were fully dissolved in water at 65 °C, NiSO₄ crystals were slowly added into the solution until a small excess amount of NiSO₄ remained present in the solution and did not dissolve even after 15 min stirring. The total amount of solid NiSO₄ crystals used was recorded and used for the solubility

data. The whole process was monitored visually in order to determine when the fully saturated, impure NiSO₄ solution at 65 °C was achieved. Solution pH was then measured with a pH electrode connected to a multi-parameter analyzer (Consort C3050).

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The saturated solution was subsequently transferred to a jacketed reactor equipped with a thermostat (Eco RE 630, Lauda). An external temperature probe was immersed into the solution and used to thermostatically control the solution. The solution was kept mixed using a marine type mixer with a 3-blade propeller at 500 rpm during the whole crystallization process. Initially, the solution was heated up to 70 °C and kept stirred for 15 min in order to dissolve all the solid particles present. Then three different cooling profiles (1, 2 and 4 hours) were employed to cool down the solution to 25 °C. During the cooling procedure, 0.5 g NiSO₄ seed crystals with a size range of 53 to 250 μ m - prepared with sieves - were added when solution temperature reached 65 °C. At the end, the suspension was kept mixed and stabilized at 25 °C for 30 min. Fig. 1 shows the schematic diagram of the cooling crystallization experimental set-up. The crystals were separated from the clear filtrate by vacuum filtration with a Büchner funnel and crystals were dried at room temperature for three days. Fig. 2 illustrates the temperature profiles of cooling crystallization.

(Figure 1)

(Figure 2)

2.3 Characterization

The crystals obtained from batch cooling crystallization were characterized by X-ray powder diffraction (XRD, X'Pert PRO) using a cobalt radiation source ($\lambda_{k\alpha_1}$ =1.7890 Å) operated at 40 kV with 40 mA and scans were made over a 2ϑ range of $10-120^\circ$ with a step size of 0.0263° . Solids were also analyzed with a Raman spectroscopy (PicoRaman, Timegate Instrument Oy) equipped with a 532 nm picosecond pulsed laser. A BWTek sampling probe was used to capture the Raman signal from particles and three Raman spectra were captured for each sample with three different focal points in order to acquire a more representative signal over a large sampling area. Spectral data was then averaged to provide the typical Raman response for each crystallization product. The morphology of the crystals was photographed with an optical microscopy (Leica DM750) and a particle size analyzer (Malvern Mastersizer 3000) was used to determine particle size distribution (PSD). It was examined that the obtained NiSO₄ crystals were insoluble in pure ethanol (99.9%, ALTIA Oyj) and consequently, the pure ethanol was selected as a background solvent to be used for PSD analysis. Samples were prepared with a mixture of ethanol and solids in order to disperse the crystals. Prior to analysis, sample bottles were sonicated in an ultrasonic water bath for 2 min. The container and apparatus of the Mastersizer were washed with distilled water several times before use and subsequently rinsed with pure ethanol a number of times between each analysis. A Fraunhofer mathematical model was applied to analyze PSD. Moisture of the crystals was measured via a gravimetric methodology. Purity of the crystals present in the unwashed NiSO₄ crystals was analyzed using a combined total dissolution and inductively coupled plasma optical emission spectroscopy (ICP-OES, Thermo Electron iCAP 6500 Duo) protocol, whereas the Cl content in the crystals was analyzed by Ion Chromatography (IC, Dionex ICS-2000).

3. Results and discussion

3.1 Solubility of NiSO₄ in complex impure systems

Generally, the presence of electrolyte ions as impurities have considerable effects on the solubility of the main compound as it can either increase or reduce the solubility in the solvent. In the present study, there are several electrolyte ions such as Ni²⁺, Cl⁻, SO₄²⁻, Mg²⁺ and Na⁺, and sulfuric acid within the solution. In particular, the acidic nickel-rich solution from the electrowinning process contains a high concentration of chloride, so the impact of chloride ions on the solubility of nickel sulfate was

deemed to be of most interest. Fig. 3 presents the solubility of NiSO₄ as a function of the mass ratio of Cl^{-}/SO_{4}^{2-} at 65 °C and the results indicate that an increase in the ratio of Cl^{-}/SO_{4}^{2-} decreases the solubility of NiSO₄ in the water. Nevertheless, it is worth noting that during the solution preparation phase, observation of the crystals in the solution was challenging since the color of the solution was dark green. Consequently, there may be some deviations in the solubility data resulting from the visual observation utilized to ensure the slight excess of solids in the solution.

(Figure 3)

3.2 Cooling crystallization of NiSO₄

From the pH measurements it was found that all the solutions before and after cooling crystallization had a pH range between 0.2 to 1.3. Impurities can have considerable effects on the crystal growth as their presence can either promote or suppress depending on how these impurities affect the supersaturation degree through changes in the solution properties and equilibrium concentration. Moreover, as the structure of the crystals and crystal habit can also be altered by impurities, it is important to investigate the crystal properties obtained from various impure solutions [10]. Typical XRD patterns of all the crystals obtained from 1 h cooling crystallization are shown in Fig. 4a. As there are numerous peaks present in nickel sulfate crystals, there is a significant challenge to identify the phase composition. The XRD analysis report for each sample was obtained using HighScore software and most of the characteristic peaks were examined visually with comparison to the reference data to determine the final crystal phase composition. With the exception of Sample 7, all samples correlate with reference data ICDD 00-047-1811, which indicates that nickel sulfate hexahydrate (NiSO₄· $6H_2O$) mainly crystallized from the solutions. The XRD pattern of Sample 7 on the other hand, was found to be consistent with ICDD 00-033-0955, which although it correlates with the formation of the same compound of NiSO₄·6H₂O it possesses a different crystal arrangement; Sample 7 is monoclinic, whereas the majority possesses a tetragonal crystal structure. This phenomenon was also observed in the Raman analysis as presented in Fig. 4b. Most of the samples have the same characteristic peak located at a Raman shift of 982 cm⁻¹, whereas Sample 7 has the shift centered on 979 cm⁻¹. Nickel sulfate hexahydrate can be crystallized in two polymorphs, namely α -NiSO₄·6H₂O and β -NiSO₄·6H₂O, which have tetragonal and monoclinic crystals respectively [12]. Petrova et al. [13] reported that α -NiSO₄·6H₂O has Raman characteristic peak of 983 cm⁻¹, from which it can be deduced that a majority of the crystals obtained from the cooling crystallization are tetragonal α - $NiSO_4 \cdot 6H_2O$.

(Figure 4)

For the other two cooling rates investigated (cooling time of 2 and 4 hrs, respectively) Sample 6 was observed to be different to the other samples according to the XRD and Raman analyses. This suggests that under these cooling regimes, it is Sample 6 that crystallizes as monoclinic NiSO₄· $6H_2O_7$, whilst the other samples comprise of tetragonal α -NiSO₄·6H₂O. Due to high amount of chloride in the initial solutions of Sample 6 and 7, nickel chloride might be present as an impurity in the crystals, although Raman was unable to detect chloride. Generally, NiSO₄·7H₂O can be crystallized from pure water below 31.5 °C, and above this temperature the crystals of α -NiSO₄·6H₂O appear and transform to the β form at 53.3 °C. Frondel et al. [14] have also stated that retgersite (tetragonal α -NiSO₄·6H₂O) can be formed at temperatures at least as low as 0 °C from the solutions that contain sulfuric acid. In the current research, nickel sulfate hexahydrate was mainly crystallized from cooling crystallization. This may due to the presence of acid and several impurities in the system that affects the solubility and crystal kinetics. Crystal shape differences can be clearly seen in Fig. 5, which were taken with an optical microscope. The crystals of Sample 7 obtained from the 1 hour cooling crystallization (Fig. 5b) and the crystals of Sample 6 obtained from 2 and 4 hours batch cooling crystallization have elongated crystals, whereas the other samples comprise of small cubic shape crystals (Fig. 5a and c). The phenomenon displayed in Fig. 5 are consistent with the findings observed from XRD and Raman

analysis. As previously reported in literature [15], Raman is capable of identifying crystal polymorphs and hydrate forms. From the results presented here, it is clear that the high concentration of chloride present in the solution had an effect on the crystal kinetics, which lead to the observed differences in crystal structure.

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(Figure 5)

All crystal samples were found to be easy to separate from the mother liquor by vacuum filtration. The moisture of all the filtered samples were determined by gravimetric method and the results show that the average water content of the samples obtained from cooling time 1, 2 and 4 hours was 9, 7 and 4%, respectively. Moisture level of the filter cake is crucial for the final purity of the crystalline product, especially when the mother liquor has a high impurity concentration. In this case, the mother liquor remnants in the filter cake could be rinsed away by washing. The results suggest that the overall water content in the filter cake samples decreased with the decrease in cooling rate i.e. with longer cooling time, a lower filter cake moisture can be achieved. It was also evident that drying of filter cakes was much easier with samples obtained at the lower cooling rates. The particle size distributions of all the samples were also analyzed, however, the results were deemed unreliable due to strong crystal agglomeration and rock-type filter cake formation, as highlighted by the microscopy images shown in Fig. 5. In addition, the crystals did not disperse well in the background solution (ethanol) - even with ultra-sonication - as a result, significant errors were introduced that are not reflective of the real particle size of the samples. The formation of agglomerates is complex and many factors have an impact like particle size, particle shape and moisture, solubility as well as ion concentration conditions [16, 17].

The concentration of Ni in each clear filtrate solution obtained from 1 h cooling crystallization was analyzed with atomic absorption spectroscopy (AAS). Together with the solubility data shown in Fig. 3, the yield for each sample was calculated based on the Ni concentration, which gave an average value 696 g NiSO₄· $6H_2O$ in 1 kg of water. The concentration of Ni, S, and impurities such as Mg and Na present in the crystals were determined by ICP-OES. Together with the results of Cl concentration obtained by IC and the moisture content, the purity of the NiSO₄·6H₂O crystals obtained were calculated based on the sulfur concentration and are shown in Fig. 6. The retained mother liquor quantity after filtration in the unwashed crystals was also taken into account based on the results from the moisture measurements. It can be clearly seen that the purity of the crystals decreased with the increase of the mass ratio of Cl^{-}/SO_{4}^{2-} . Except for the sample with the highest concentration of Cl obtained from the 2 h batch cooling time, the other unwashed final products have purities greater than 93%. Nevertheless, the cooling rate does not appear to have a significant influence on the final crystal purity. A comparison of the initial concentration of Mg, Na and Cl in solution with those in the final crystals found that between 84 – 99% of Mg, 16 – 48% Na and 1 – 36% Cl remained in the crystals (Fig. 7). These results indicate that Mg is the most difficult element to remove from the crystals, possibly because of the similarity in chemical and physical properties of nickel and magnesium [18], although washing could be employed to improve the crystal purity in further research work.

(Figure 6)

(Figure 7)

4. Conclusions

Batch cooling crystallization was successfully employed to recover nickel as a nickel sulfate salt from synthetic acidic nickel-rich solutions that mimic industrial process streams with impurities such as Na, Mg and Cl. Nickel sulfate hexahydrate was predominantly crystallized as tetragonal α -NiSO₄·6H₂O, with cubic shape crystals when temperature was decreased from 70 to 25 °C. In contrast, the elongated crystals crystallized in the second-highest concentrated chloride solution from 1 h cooling

crystallization, and in the highest concentrated chloride solution from 2 h and 4 h cooling crystallization. It means that the β -NiSO₄·6H₂O crystals were obtained from cooling crystallization when a high amount of chloride was present in the solution as this affects the crystal growth kinetics. Furthermore, it also appears that cooling rate has an impact on the formation of β -NiSO₄·6H₂O crystals since it can cause different degrees of supersaturation. In this current research, the hexahydrate form was only crystallized after cooling to 25 °C, which is in contrast to the results found in literature that indicate NiSO₄·7H₂O is stable in water below 31 °C. As the presence of both acid and impurities affect polymorph formation, further research is needed to investigate how to control the polymorph formation and to determine if polymorph transformation occurs during cooling crystallization. Additionally, the results demonstrated that an increase of the chloride to sulfate ratio reduces the solubility of NiSO₄ in impure acidic solutions and decreases the subsequent purity of NiSO₄· $6H_2O$ crystals obtained. Nonetheless, the findings also showed that cooling rate did not have any notable impact on crystal purity as it had little effect on crystal polymer formation. Lower cooling rates also resulted in a reduction of the associated crystal moisture, although the level of remaining impurities varied depending on the ion: Mg > Na > Cl. Strong agglomeration was observed to occur in the crystals.

Overall, the research clearly highlights that cooling crystallization can be used as a feasible way to recover nickel as inorganic salts from industrial acidic multi-component solutions as NiSO₄·6H₂O crystals with purity > 93% can be obtained by cooling crystallization. Nevertheless, more research is required in order to obtain battery grade NiSO₄ and based on the results outlined here, some suggestions are proposed to improve future crystal purity. First, much lower cooling rates such as 5 °C/h could be utilized for cooling crystallization since lower moisture content can be obtained with lower cooling rates. In addition, more uniform crystals may be obtained through slow cooling procedure and this would minimize aggregation formation. Second, washing is needed to remove mother liquor remnants from the crystal, although it should be confirmed that any washing procedure used does not affect the crystal polymorphs. Finally, use of inline tools would allow the virtual examination or real time monitoring the cooling crystallization process. These would provide valuable insight into real time changes and additional data to help understand the behavior of the impurities and to identify operating parameters in order to better control the crystallization process. The crystal purity and size distribution will be improved and precisely controlled with enhanced accurate and reliable information.

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Symbols used

Abbreviations

| AAS | Atomic absorption spectroscopy |
|---------|------------------------------------------------------------|
| IC | lon chromatography |
| ICP-OES | Inductively coupled plasma - optical emission spectroscopy |
| PSD | Particle size distribution |
| XRD | X-ray powder diffraction |

References

[1] Bloomberg New Energy Finance, Electric Vehicle Outlook 2017, https://data.bloomberglp.com/bnef/sites/14/2017/07/BNEF_EVO_2017_ExecutiveSummary.pdf (Accessed on October 9, 2018)

[2] M. Aaltonen, C. Peng, B.P. Wilson, M. Lundström, *Recycling* **2017**, *2*(*4*), 20. DOI: 10.3390/recycling2040020

[3] B. Han, A. Porvali, M. Lundström, M. Louhi-Kultanen, *Chem. Eng. Technol.* **2018**, *41(6)*, 1205-1210. DOI: 10.1002/ceat.201700667

[4] B.P. Wilson, N.P. Lavery, D.J. Jarvis, T. Anttila, J. Rantanen, S.G.R. Browne, N.J. Adkins, *J. Power Sources* **2013**, *243*, 242–252. DOI: https://doi.org/10.1016/j.jpowsour.2013.05.186

[5] V. Coman, B. Robotin, P. Ilea, *Resour. Conserv. Recycl.* **2013**, *73*, 229–238. DOI: https://doi.org/10.1016/j.resconrec.2013.01.019

[6] T. Shi, S. Zou, J. Liu, L. Zuo, C. Lv, S. Jia, R.L. Qiu, *J. Civil Environment Eng.* **2011**, *1:103*, 1-7. DOI:10.4172/2165-784X.1000103

[7] G.A. Moldoveanu, G.P. Demopoulos, *JOM* **2002**, *54*, 49–53. DOI: https://doi.org/10.1007/BF02822606

[8] J.Y. Lee, S.V. Rao, B.N. Kumar, D.J. Kang, B.R. Reddy, *J. Hazard. Mater.* **2010**, *176*, 1122–1125. DOI: https://doi.org/10.1016/j.jhazmat.2009.11.137

[9] www.palminc.com (Accessed on October 9, 2018)

[10] J.W. Mullin, *Crystallization*, 4th ed., Butterworth-Heinemann, Oxford **2001**.

[11] A. Seidell, *Solubility of inorganic and metal organic compounds*, 3rd ed., vol. 1, D. Van Nostrand company, Inc., New York **1940**.

[12] D. Krishnamurti, *Proc. Indian Acad. Sci.* **1958**, *48(6)*, 355–363. DOI: https://doi.org/10.1007/BF03052920

[13] E.V. Petrova, M.A. Vorontsova, V.L. Manomenova, L.N. Rashkovich, *Crystallogr. Rep.* **2012**, *57*, 579–584. DOI: https://doi.org/10.1134/S1063774512010099

[14] C. Frondel, C. Palache, Am. Mineral. **1949**, 34(3-4), 188–194.

[15] M. Gotić, M. Ivanda, S. Popović, S. Musić, *Mater. Sci. Eng. B* **2000**, *77*(*2*), 193–201. DOI: https://doi.org/10.1016/S0921-5107(00)00488-8

[16] A. Vertanessian, *J. Mater. Res.* **2003**, *18*(*2*), 495–506. DOI: https://doi.org/10.1557/JMR.2003.0063

[17] E. Simone, R. Othman, G.T. Vladisavljević, Z.K. Nagy, *Pharmaceutics* **2018**, *10(1)*, 17. DOI: 10.3390/pharmaceutics10010017

[18] H. McCoy, M.A. Kenney, Magnesium Res. 1992, 5 (3), 223–232.

Tables:

Table 1. Composition of the studied impure acidic solutions for cooling crystallization.

| Exporimont No | NiCl ₂ | H ₂ SO ₄ | MgCl ₂ | NaCl |
|----------------|--------------------|--------------------------------|--------------------|--------------------|
| experiment No. | $(g g^{-1} H_2 O)$ | $(g g^{-1} H_2 O)$ | $(g g^{-1} H_2 O)$ | $(g g^{-1} H_2 O)$ |
| #1 | 0.025 | 0.099 | 0 | 0 |
| #2 | 0.043 | 0.069 | 0 | 0 |
| #3 | 0.195 | 0.073 | 0 | 0 |
| #4 | 0.237 | 0.120 | 0.005 | 0.005 |
| #5 | 0.363 | 0.082 | 0.005 | 0.005 |
| #6 | 0.471 | 0.074 | 0.004 | 0.003 |
| #7 | 0.424 | 0.088 | 0.004 | 0.004 |
| #8 | 0.078 | 0.024 | 0.002 | 0.010 |

Figures:



Fig. 1 Schematic diagram of the cooling crystallization experimental set-up.



Fig. 2 Temperature profiles of cooling crystallization.



Fig. 3 Effect of mass ratio of Cl^{-}/SO_4^{2-} on NiSO₄ solubility in impure acidic solutions at 65°C. Experimental conditions are expressed by number in each data point.



Fig. 4 XRD patterns (a) and Raman spectra (b) of the samples from 1 h cooling crystallization. Legends in the magnified picture in Fig. 4b are the same as shown in the normal figure, i.e. light blue curve stands for Exp 7.



Fig. 5 Selected optical microscope images of the NiSO₄· GH_2O samples for Sample 6 (a), Sample 7 (b) and Sample 8 (c) obtained at 1 hour cooling crystallization.







Fig. 7 Impurities of Mg (a), Na (b), and Cl (c) remained in crystal products related to initial solution impurity as a function of the mass ratio of Cl^{-}/SO_{4}^{2-} with three different cooling rates.

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Research Article: Batch cooling crystallization was successfully applied to recover nickel as NiSO₄ crystals from acidic multicomponent solutions that mimic electrowinning downstream process solutions. High concentration of chloride reduced NiSO₄ solubility and decreased the crystal purity. Magnesium persistently remained in the crystals and was harder to remove than the other two impurities: Na and Cl.

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