Recovery of ammonium alum from waste solutions with a varying ratio of NH$_4$ to Al in groundwater remediation after underground uranium leaching

V. Hostomská, J. Hostomský *

Institute of Inorganic Chemistry, Academy of Sciences of the Czech Republic, 250 68 Řež, Czech Republic

Abstract

Experiments with cooling crystallization of ammonium alum, $(NH_4Al(SO_4)_2 \cdot 12H_2O)$, were performed with concentrated multicomponent acidic solutions (originating from underground uranium leaching in Stráž pod Ralskem area, Czech Republic, and containing as the principal components Al^{3+}, NH_4^+, and SO_4^{2-} ions) as well as with similar solutions prepared in the laboratory. The yield of $NH_4Al(SO_4)_2 \cdot 12H_2O$ crystals increased significantly with the increasing NH_4^+/Al^{3+} molar ratio, in accordance with pertinent solubility data. The purifying effect of crystallization was quantified by means of the distribution coefficients, characterizing the uptake of ionic impurities to alum crystals; the tendency of cationic impurities to crystallize with $NH_4Al(SO_4)_2 \cdot 12H_2O$ decreased in the following order: $K^+ \gg Cr^{3+} > Na^+ \approx Fe^{3+} > Mg^{2+} \approx Zn^{2+} > Fe^{2+}$. Additionally, gypsum $(CaSO_4 \cdot 2H_2O)$ solubilities at 25 °C, in mother liquors after $NH_4Al(SO_4)_2 \cdot 12H_2O$ crystallization, were determined.
© 2007 Elsevier B.V. All rights reserved.

Keywords: Ammonium aluminium sulphate; Gypsum; Crystallization; Solubility; Impurity; Distribution

1. Introduction

From 1967 to 1996, the technique of in situ underground leaching was used to extract uranium from permeable uranium-bearing sandstone formations at the Stráž pod Ralskem area (Czech Republic). In situ leaching (or 'solution mining') involves injection of leaching solution down a group of boreholes into the ore body, and pumping of the pregnant solution to the surface for uranium recovery in ion exchange columns [1]. After reagent make-up, the effluent solution is recycled for further leaching. At the Stráž pod Ralskem site, leaching by concentrated sulphuric acid solutions has been used, and a total of approximately 4 million metric tons of H_2SO_4 has been delivered to the uranium-bearing strata. Implementation of internationally accepted criteria and standards of waste management practices together with specific environmental concerns (a threat of contamination of major underground drinking water reservoirs) have led in the early 1990s to the decision to phase out in situ leaching processes in the Stráž pod Ralskem area, and to

start a complex long-term environmental restoration programme which will include desalination of contaminated acidic underground solutions. The clean-up efforts are expected to continue for at least 35 years [2].

The principal components of the underground solutions are free sulphuric acid and aluminium, ammonium, and sulphate ions. Furthermore, at least 30 other ions were identified as minor constituents or trace impurities. By evaporation of water in multiple-effect evaporators (already in operation), the underground solutions are made saturated with respect to ammonium aluminium sulphate dodecahydrate, ammonium alum $(NH_4Al(SO_4)_2 \cdot 12H_2O)$, which is then crystallized in continuous-flow adiabatic vacuum crystallizers. The crystallization plant (with the annual production capacity of 170,000 metric tons of $NH_4Al(SO_4)_2 \cdot 12H_2O$) was licensed for operation, but until a tailing facility for further concentration and disposal of depleted mother liquors from crystallization is built, the production of $NH_4Al(SO_4)_2 \cdot 12H_2O$ is low; the mother liquors are mixed with mining solutions and recharged to the mining zone [2].

The NH_4^+/Al^{3+} molar ratio in solutions leaving the evaporation plant is approximately 0.28–0.35, that is, less than the stoichiometric value in $NH_4Al(SO_4)_2 \cdot 12H_2O$. Therefore, the

---

* Corresponding author. Tel.: +420 266 172 183; fax: +420 220 941 502.
  E-mail address: hostomsky@iic.cas.cz (J. Hostomský).

Table 1
Composition of synthetic solutions

	Solution					
	A 0.29[a]	B 0.5[a]	C 0.7[a]	D 0.9[a]	E 0.95[a]	F 1.0[a]
Concentration $y_{0,i}$ (g/kg solution)						
NH_4^+	4.8	8.1	11.3	14.4	15.1	15.9
Al^{3+}	24.5	24.3	24.1	23.9	23.8	23.8
SO_4^{2-} (total)	206	214	220	227	229	231
H_2SO_4	47	47	47	46	46	46
Cr^{3+}	0.051	0.051	0.050	0.050	0.050	0.050
Fe^{2+}	8.9	8.8	8.8	8.7	8.7	8.7
K^+	0.26	0.25	0.25	0.25	0.25	0.25
Mg^{2+}	0.21	0.20	0.20	0.20	0.20	0.20
Na^+	0.066	0.066	0.065	0.065	0.065	0.064
Zn^{2+}	0.28	0.27	0.27	0.27	0.27	0.27

[a] NH_4^+/Al^{3+} molar ratio.

$NH_4Al(SO_4)_2 \cdot 12H_2O$ yield can be increased by addition of ammonium ion to the solution entering the crystallization unit. Equilibrium solubility data concerning these multicomponent systems are not available in literature.

$NH_4Al(SO_4)_2 \cdot 12H_2O$ is often used as an important intermediate material for the production of pure aluminium compounds such as alumina or aluminium sulphate [3–9]. Therefore, an important aspect in defining the product quality is the purity of the $NH_4Al(SO_4)_2 \cdot 12H_2O$ crystals, influenced primarily by the uptake of foreign ions from the solution into the alum lattice.

The purpose underlying the present work is to facilitate the recovery of $NH_4Al(SO_4)_2 \cdot 12H_2O$ by crystallization in the groundwater remediation after in situ uranium leaching. Hence, the effect of ammonium ion addition (as aqueous ammonia or ammonium sulphate) upon the yield of $NH_4Al(SO_4)_2 \cdot 12H_2O$ crystals in cooling crystallization has been determined, and the uptake of cationic impurities (chromium, potassium, iron, magnesium, sodium, and zinc) into alum crystals has been investigated. The cooling crystallization experiments were carried out with two types of solution—(method I), using synthetic solutions prepared in the laboratory containing the same key components as the underground solutions concentrated by evaporation, and (method II), using process solutions collected from the evaporation unit of DIAMO, Stráž pod Ralskem. Additionally, gypsum ($CaSO_4 \cdot 2H_2O$) solubilities in process solutions with the increasing NH_4^+/Al^{3+} ratio have been determined since the $CaSO_4 \cdot 2H_2O$ scale formation is potentially a serious problem in the large-scale $NH_4Al(SO_4)_2 \cdot 12H_2O$ crystallization from multicomponent process solutions.

2. Experimental

2.1. Preparation of solutions

2.1.1. Method I—synthetic solutions

Solutions were prepared in the laboratory from analytical grade chemicals—$(NH_4)_2SO_4$, $Al_2(SO_4)_3 \cdot 18H_2O$, H_2SO_4, $Cr_2(SO_4)_3 \cdot 18H_2O$, $FeSO_4 \cdot 7H_2O$, K_2SO_4, $MgSO_4 \cdot 7H_2O$, Na_2SO_4, and $ZnSO_4 \cdot 7H_2O$ (Lachema, Czech Republic); these

materials were used as received. First, a solution with the NH_4^+/Al^{3+} molar ratio equal to 0.29 was prepared using the chemicals reported above and distilled water (solution A, Table 1). The composition of this solution corresponds to the composition of a typical solution leaving the evaporation unit of DIAMO, Stráž pod Ralskem. From solution A, a series of synthetic solutions (B–F, Table 1) with the NH_4^+/Al^{3+} molar ratio increasing from 0.5 to 1.0 was prepared by addition of ammonium sulphate. Since the ferrous ion is easily oxidized by air to ferric ion, the synthetic solutions were prepared immediately before the crystallization experiments, and care was taken to minimize the oxidation of ferrous ions.

2.1.2. Method II—process solutions

Several weeks after the experiments with crystallization of $NH_4Al(SO_4)_2 \cdot 12H_2O$ from synthetic solutions were carried out, a batch of a process solution leaving the evaporation unit was obtained from DIAMO, Stráž pod Ralskem. The composition of the solution as determined by analysis of its key components is given in Table 2, solution G. As can be seen by comparison of concentrations in Tables 1 and 2, the composition of the process

Table 2
Composition of process solutions (solutions H, I, and J prepared from the stock solution G by addition of aqueous ammonia solution)

	Solution			
	G 0.34[a]	H 0.49[a]	I 0.74[a]	J 0.99[a]
Concentration $y_{0,i}$ (g/kg solution)				
NH_4^+	4.9	6.9	10.3	13.5
Al^{3+}	21.3	21.2	20.9	20.7
SO_4^{2-} (total)	180	179	177	174
H_2SO_4	36	30	20	11.5
Cr^{3+}	0.055	0.055	0.054	0.053
Fe^{3+}	7.3	7.3	7.2	7.1
K^+	0.24	0.24	0.23	0.23
Mg^{2+}	0.19	0.19	0.18	0.18
Na^+	0.064	0.063	0.062	0.062
Zn^{2+}	0.25	0.25	0.25	0.24

[a] NH_4^+/Al^{3+} molar ratio.

solution G (Table 2) corresponded fairly well to the synthetic solution A (Table 1), which served as the initial solution for preparation of the other synthetic solutions; the notable exception was the oxidation state of iron which was +3 in the process solution (only 1.4% of total iron was in the oxidation state +2 as determined by permanganate titration).

From the stock solution G with the NH_4^+/Al^{3+} molar ratio equal to 0.34, the solutions denoted as H, I, and J (Table 2) with the NH_4^+/Al^{3+} molar ratio equal to 0.49, 0.74, and 0.99, respectively, were prepared by addition of calculated quantities of concentrated aqueous ammonia solution (26 mass% NH_3, analytical grade, Lachema). In contrast to Method I, ammonium sulphate necessary for $NH_4Al(SO_4)_2 \cdot 12H_2O$ crystallization was thus produced by the reaction of ammonia with sulphuric acid present in the process solution. The advantage of ammonia addition in comparison with ammonium sulphate addition is given by the fact that the sum of total dissolved solids in the mother liquors after crystallization is lower than in the case of ammonium sulphate addition. On the other hand, ammonium sulphate addition is a more general procedure, since it can also be used with solutions, which do not contain a sufficient amount of sulphuric acid.

2.2. Crystallization of $NH_4Al(SO_4)_2 \cdot 12H_2O$

The selected solution was heated to 60 °C to dissolve the solids; 200 cm^3 volume of homogeneous solution was transferred to a magnetically stirred closed glass vessel, and cooled from 60 to 25 °C without seeding at a linear cooling rate equal to 0.2 °C/min. Suspension of crystals was then kept at 25 ± 0.1 °C for 4 h; in preliminary experiments it was established that the Al^{3+} and NH_4^+ concentrations remained constant within experimental uncertainty (±2%) already after approximately 1–2 h. The stirring operation was ceased, and the thermostated system was, then, allowed to settle down for at least 1 h. A sample of the clear solution was pipetted for chemical analysis. The solid phase was separated by filtration under vacuum, washed successively with cold water and ethanol, dried at a room temperature, and subjected to chemical, and X-ray powder diffraction (XRD) analyses. The rest of the mother liquor was used for determination of $CaSO_4 \cdot 2H_2O$ solubility by equilibrating the solution with $CaSO_4 \cdot 2H_2O$ crystals in a thermostated shaking bath for 8 h [10].

2.3. Analytical methods

Samples of solutions and crystals were analysed for Al, Cr, Fe, K, Mg, Na, and Zn by atomic absorption spectrophotometry using a Varian SPECTR AA880 instrument. Sulphate concentrations were determined by a gravimetric method (weighing $BaSO_4$ after precipitation with a $BaCl_2$ solution), and ammonium concentrations were determined by a distillation method (ammonia liberated from the solution sample by NaOH was absorbed in a known volume of a standardized HCl solution).

Pulverised crystalline products were analysed by a Siemens D5005 XRD analyzer. The diffraction patterns were compared with the data listed in the Powder Diffraction File [11].

2.4. Yield of $NH_4Al(SO_4)_2 \cdot 12H_2O$

Yields of $NH_4Al(SO_4)_2 \cdot 12H_2O$ crystals, η_{cryst}, defined as the mass of crystals obtained from a unit mass of solution, were calculated from the initial and final concentrations of ammonium ion. The mass balance of ammonium ion in the crystallization process gives

$$y_{cryst,NH_4} \eta_{cryst} = y_{0,NH_4} - (1 - \eta_{cryst}) y_{1,NH_4} \quad (1)$$

where y_{0,NH_4}, y_{1,NH_4} are the concentrations of ammonium ion in the solution before crystallization, and in the mother liquor after crystallization (g NH_4^+/kg solution), respectively, and $y_{cryst,NH_4} = 1000 M_{NH_4}/M_{NH_4Al(SO_4)_2 \cdot 12H_2O}$ is the concentration of NH_4^+ ions in alum crystals (g NH_4/kg crystals); M_{NH_4}, $M_{NH_4Al(SO_4)_2 \cdot 12H_2O}$ are the respective molar masses. Then the crystal yield is equal to

$$\eta_{cryst} = \frac{y_{0,NH_4} - y_{1,NH_4}}{y_{cryst,NH_4} - y_{1,NH_4}} \quad (2)$$

The mass of ammonium ion remaining in the mother liquor produced from a unit mass of the initial solution, m_{NH4}, is equal to

$$m_{NH_4} = y_{1,NH_4}(1 - \eta_{cryst}) = y_{1,NH_4} \frac{y_{cryst,NH_4} - y_{0,NH_4}}{y_{cryst,NH_4} - y_{1,NH_4}} \quad (3)$$

The ratio of solution masses before and after crystallization, f, is equal to

$$f = \frac{1}{1 - \eta_{cryst}} = \frac{y_{cryst,NH_4} - y_{1,NH_4}}{y_{cryst,NH_4} - y_{0,NH_4}} \quad (4)$$

Concentration of solution components, which do not enter into crystals (e.g., H_2SO_4), is thus increased by the factor of f.

3. Results and discussion

3.1. Concentrations of NH_4^+, Al^{3+}, and SO_4^{2-} in mother liquor after crystallization, and the yields of $NH_4Al(SO_4)_2 \cdot 12H_2O$

The only crystalline phase which was identified in the products of crystallization by the XRD analysis was $NH_4Al(SO_4)_2 \cdot 12H_2O$ (tschermigite); the XRD patterns of the products agreed well with the literature [11].

Concentrations of the constituent components of $NH_4Al(SO_4)_2 \cdot 12H_2O$ in the mother liquors at the final temperature of 25 °C after crystallization of $NH_4Al(SO_4)_2 \cdot 12H_2O$ from the synthetic, and process solutions are given in Table 3. The NH_4^+ and Al^{3+} concentrations are also visualised in a condensed form in Fig. 1.

In Fig. 2, it is shown that the concentrations of ammonium and aluminium ions in mother liquors after crystallization are in a good agreement with the solubilities of $NH_4Al(SO_4)_2 \cdot 12H_2O$ at 25 °C in the quaternary system $(NH_4)_2SO_4–Al_2(SO_4)_3–H_2SO_4–H_2O$ [10] with the H_2SO_4

Table 3
Concentrations of NH_4^+ and Al^{3+} in mother liquors and yields of $NH_4Al(SO_4)_2 \cdot 12H_2O$ in crystallization from synthetic and process solutions with different NH_4^+/Al^{3+} ratios

Experiment	Solution	NH_4^+ molar ratio before crystallization	y_{1,NH_4}	$y_{1,Al}$	η_{cryst}
			NH_4^+ in mother liquor (g/kg solution)	Al^{3+} in mother liquor (g/kg solution)	Yield of $NH_4Al(SO_4)_2 \cdot 12H_2O$ (kg/kg solution)
Synthetic solutions					
1	A	0.29	1.60	16.8	0.084
2	B	0.50	2.30	14.5	0.155
3	C	0.70	3.12	11.1	0.217
4	D	0.90	4.63	8.65	0.277
5	E	0.95	5.32	8.60	0.285
6	F	1.00	5.50	8.18	0.304
Process solutions					
7	G	0.34	1.46	17.4	0.090
8	G	0.34	1.59	17.7	0.087
9	G	0.34	1.50	17.7	0.089
10	H	0.49	1.83	14.8	0.133
11	H	0.49	1.89	15.7	0.132
12	H	0.49	2.05	16.4	0.128
13	H	0.49	2.05	16.2	0.128
14	I	0.74	3.17	11.9	0.193
15	I	0.74	3.17	11.7	0.193
16	I	0.74	2.46	12.5	0.209
17	J	0.99	5.41	8.3	0.235
18	J	0.99	5.05	8.6	0.243

mass fraction on a salt-free basis equal to 0.1 (approximately 70–90 g H_2SO_4/kg solution). According to the phase rule, the above system (with a fixed H_2SO_4 concentration) has one degree of freedom; consequently, equilibrium concentrations of NH_4^+ and Al^{3+} at 25 °C are related by a functional relationship represented by a curve in Fig. 2 [10]. In the recent study of the authors [10], it has been found that the $NH_4Al(SO_4)_2 \cdot 12H_2O$ solubilities in the above quaternary system at 25–50 °C are only moderately influenced by the sulphuric acid concentra-

tion up to approximately 90 g H_2SO_4/kg solution. The H_2SO_4 concentrations in the crystallization experiments in the present work varied from 11 to 47 g H_2SO_4/kg solution because of ammonia addition to process solutions or – in experiments with synthetic solutions – due to the concentrating effect of crystallization upon the noncrystallizing solutes according to Eq. (4). It can be stated that sulphuric acid and minor com-
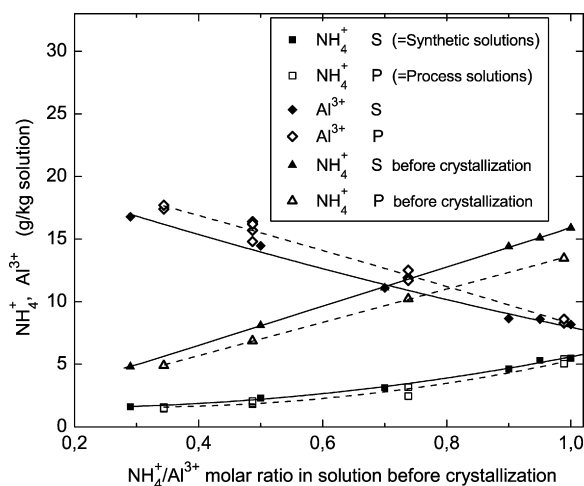

Fig. 1. The effect of the NH_4^+/Al^{3+} molar ratio in solution before crystallization upon the final concentration of ammonium and aluminium ions in mother liquors after crystallization of $NH_4Al(SO_4)_2 \cdot 12H_2O$ from synthetic and process solutions. The NH_4^+ concentrations in solutions before crystallization are also plotted.

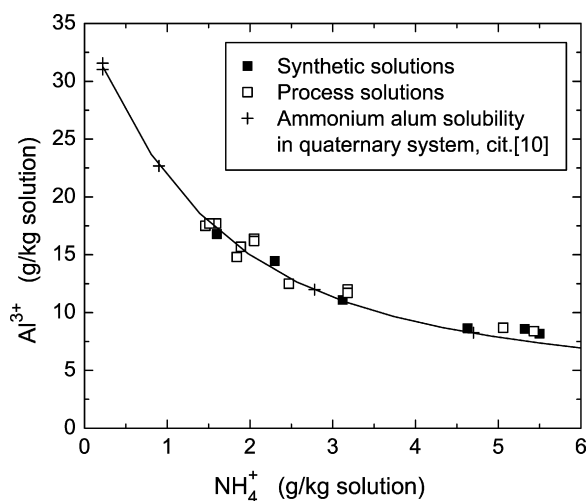Fig. 2. The relationship between the concentrations of NH_4^+ and Al^{3+} in mother liquors after crystallization of $NH_4Al(SO_4)_2 \cdot 12H_2O$ from synthetic and process solutions. For comparison, the curve and points (+) represent the relationship between the concentrations of NH_4^+ and Al^{3+} in a solution in equilibrium (at 25 °C) with alum crystals in the quaternary $(NH_4)_2SO_4–Al_2(SO_4)_3–H_2SO_4–H_2O$ system where the H_2SO_4 mass fraction on the salt-free basis is equal to 0.1 [10].
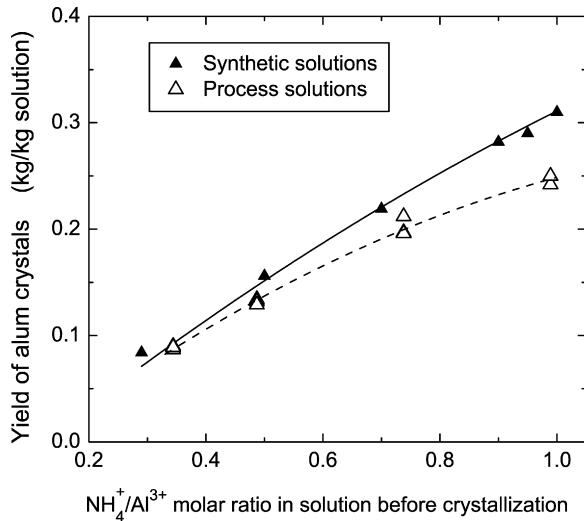
Fig. 3. Yields of $NH_4Al(SO_4)_2 \cdot 12H_2O$ for crystallization from synthetic and process solutions calculated according to Eq. (2) and plotted vs. the NH_4^+/Al^{3+} molar ratio in solution before crystallization (the yields are related to 1 kg of solution before crystallization).
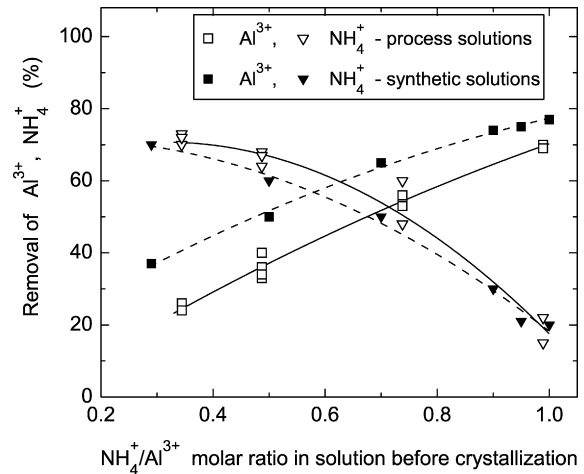

Fig. 4. Removal of ammonium and aluminium ions related to the initial solution A or G, respectively (that is, to the solution before the ammonium ion addition) as a function of the NH_4^+/Al^{3+} molar ratio in solution before crystallization.

ponents present in the solutions do not affect substantially the $NH_4Al(SO_4)_2 \cdot 12H_2O$ solubility in mother liquors and, therefore, the solubility of $NH_4Al(SO_4)_2 \cdot 12H_2O$ in mother liquors originating from process solutions of similar compositions as those in Table 2 may be estimated from data for the $(NH_4)_2SO_4$–$Al_2(SO_4)_3$–H_2SO_4–H_2O quaternary system [10]. For temperatures lower than 25 °C, interpolation using also the data for the $(NH_4)_2SO_4$–$Al_2(SO_4)_3$–H_2O ternary system at 0 °C [12] could give a rough estimate.

The yield of $NH_4Al(SO_4)_2 \cdot 12H_2O$ crystals plotted as a function of the NH_4^+/Al^{3+} molar ratio in the solution before crystallization is given in Fig. 3. It is apparent that the yields increase significantly with increasing addition of ammonium ion (in the form of ammonium sulphate or ammonia); if the NH_4^+/Al^{3+} ratio is increased from 0.29 to 1.00, the yield of crystals from the synthetic solutions increases by the factor of 3.6 whereas by increasing the NH_4^+/Al^{3+} ratio from 0.34 to 0.99 in the process solutions, the crystal yield is increased by the factor of 2.7.

The yield of alum crystals is generally a monotonously increasing function of the addition of ammonium sulphate or aqueous ammonia to the initial solutions (A, G in Tables 1 and 2), respectively. Due to the very low solubility of $NH_4Al(SO_4)_2 \cdot 12H_2O$ at high NH_4^+ concentrations (Fig. 2), almost complete recovery of aluminium ions can be theoretically achieved. In desalination of waste solution from underground uranium leaching, however, the mass of ammonium ions remaining in the mother liquor after crystallization must not be greater than the mass of ammonium ion in the initial solution (A, G) before the ammonium ion addition, that is, the condition

$$m_{NH_4} = y_{1,NH_4}(1 - \eta_{cryst}) \leq y'_{0,NH_4} \qquad (5)$$

must be fulfilled, where y'_{0,NH_4} is the NH_4^+ concentration in the initial solution (A, G) before the ammonium ion addition. In Fig. 4, the percentage recovery of aluminium and ammonium

ions from the initial solutions (A, G) is plotted; the percentage recovery of ammonium ion is equal to $100(1 - m_{NH_4}/y'_{0,NH_4})$, consequently, the condition given by Eq. (5) means that the ammonium ion recovery must not be negative. From Fig. 4 it follows that the condition prescribed by Eq. (5) was satisfied in all experiments, and that in processing the initial solutions A and G, the NH_4^+/Al^{3+} molar ratio of approximately 1.05 is the upper limit which should not be exceeded.

3.2. Distribution of impurities in crystallization of $NH_4Al(SO_4)_2 \cdot 12H_2O$

The purification effect of the crystallization process with respect to individual impurities is characterized by the distribution coefficient [13], which in the present context is defined as

$$D_{i,Al} = \frac{y_{cryst,i}/y_{cryst,Al}}{(y_{0,i} + y_{1,i})/(y_{0,Al} + y_{1,Al})} \qquad (6)$$

where in the denominator, there is the ratio of the average concentration of the impurity, and aluminium ions in solution, respectively (indices 0 and 1 denote the concentration before and after crystallization, respectively). The distribution coefficient defined by Eq. (6) is related to aluminium as the macrocomponent. The value of $D_{i,Al}$ is determined by both the thermodynamics and kinetics of the crystallization process. A true thermodynamic equilibrium of ions between the solid state and solution occurs only at a very large time scale, and the value of the distribution coefficient under those conditions (denoted $D_{i,Al,eq}$) represents a limiting value of the 'kinetic' (nonequilibrium) coefficient.

Concentrations of impurities in mother liquors after crystallization did not differ significantly from the concentrations in the corresponding pregnant solutions except for potassium whose concentration in mother liquor decreased from 0.23–0.26 g/kg solution to 0.08–0.12 g/kg solution. The concentrations of impu-

Table 4
Concentration of impurities in $NH_4Al(SO_4)_2 \cdot 12H_2O$ crystals

Experiment	Solution	NH_4^+/Al^{3+} molar ratio	Concentration in alum crystals (g/kg)					
			Cr^{3+}	Fe	K^+	Mg^{2+}	Na^+	Zn^{2+}
Synthetic solutions								
1	A	0.29	0.055	0.45[a]	1.90	0.017	0.023	0.019
2	B	0.5	0.051	0.57[a]	1.04	0.022	0.017	0.031
3	C	0.7	0.052	0.59[a]	0.83	0.034	0.028	0.030
4	D	0.9	0.050	0.62[a]	0.73	0.021	0.022	0.033
5	E	0.95	0.041	0.58[a]	0.62	0.023	0.027	0.030
6	F	1	0.039	0.39[a]	0.60	0.015	0.026	0.023
Process solutions								
7	G	0.34	0.033	1.6[b]	1.74	0.015	0.023	0.015
9	G	0.34	0.034	1.8[b]	1.77	0.020	0.021	0.026
10	H	0.49	0.044	3.5[b]	1.34	0.023	0.020	0.035
12	H	0.49	0.033	1.4[b]	1.35	0.021	0.019	0.028
13	H	0.49	0.031	1.2[b]	1.25	0.017	0.013	0.022
14	I	0.74	0.040	2.0[b]	0.87	0.025	0.019	0.035
16	I	0.74	0.035	1.4[b]	0.93	0.023	0.015	0.031
17	J	0.99	0.045	2.0[b]	0.66	0.030	0.029	0.044

[a] Fe^{2+}.
[b] Fe^{3+}.

rities in the crystals obtained in experiments with both types of solutions are given in Table 4. Distribution coefficients of individual impurities were calculated according to Eq. (6) and the results summarized in Fig. 5 and Table 6.

Potassium ions are capable of isomorphous substitution of ammonium ions in the ammonium alum lattice. The distribution coefficient of potassium ion, $D_{K,Al}$, decreases from the value of 3.5 at the NH_4^+/Al^{3+} molar ratio of 0.3 to 1.0 at the NH_4^+/Al^{3+} molar ratio equal to unity (Fig. 5). Thus, at the low NH_4^+/Al^{3+} molar ratios, potassium ions are preferentially incorporated into alum crystals, and by increasing the NH_4^+/Al^{3+} molar to the value close to 1.0, it is possible to reduce the potassium uptake significantly.

Cr^{3+}, Fe^{2+}, Fe^{3+}, Mg^{2+}, Na^+, and Zn^{2+} ions exhibit an approximately constant value of the distribution coefficient over the range of NH_4^+/Al^{3+} molar ratios; as an example, plot of

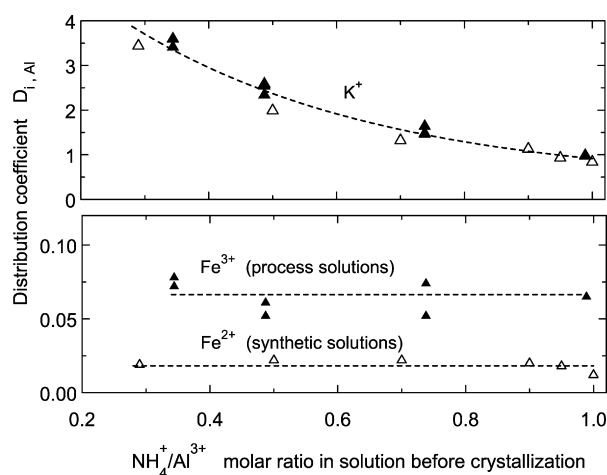the distribution coefficient for Fe^{2+} (in synthetic solutions) and Fe^{3+} (in process solutions) versus the NH_4^+/Al^{3+} molar ratio before crystallization is given in Fig. 5. Therefore, only average values of $D_{i,Al}$ for these ions are given in Table 6.

From Table 6, it is apparent that the lowest values of the distribution coefficient were obtained for Fe^{2+} in the series of experiments with synthetic solutions, where iron was added as ferrous sulphate ($D_{Fe(II),Al} = 0.018$), and for Mg^{2+} and Zn^{2+} in both types of solutions ($D_{i,Al} \approx 0.03$). The average value of the distribution coefficient for Fe^{3+} in crystallization from process solutions ($D_{Fe(III),Al} = 0.074$) is 3.7 times higher than the corresponding value of $D_{Fe(II),Al}$ for Fe^{2+} in crystallization from synthetic solutions. The value of $D_{Fe(III),Al}$ for process solutions (0.074) compares well with the values of 0.086 and 0.059 given by Gorshtein [14] for the distribution coefficient of Fe(III) in crystallization of $NH_4Al(SO_4)_2 \cdot 12H_2O$ at 20 and 30 °C, respectively. These 'kinetic' values of the distribution coefficient, $D_{Fe(III),Al}$, are, as expected, higher than the thermodynamic (equilibrium) value of the distribution coefficient for Fe(III), $D_{Fe(III),Al,eq} \approx 0.02$, estimated from the phase equilibria in the system $NH_4Al(SO_4)_2–NH_4Fe(SO_4)_2–H_2O$ at 25 °C [15], which exhibits a continuous series of solid solutions of ammonium aluminium alum and ammonium ferric alum.

3.3. Solubility of $CaSO_4 \cdot 2H_2O$ in mother liquors after crystallization of $NH_4Al(SO_4)_2 \cdot 12H_2O$ from process solutions

Equilibrium concentrations of calcium ions in mother liquors contacted at 25 °C with $CaSO_4 \cdot 2H_2O$ crystals are summarized in Table 5. The equilibrium concentrations of Ca^{2+} are plotted versus the total sulphate concentration in Fig. 6. From Table 5 and Fig. 6, it can be seen that the $CaSO_4 \cdot 2H_2O$ solubility (expressed as the Ca^{2+} concentration) in mother liquors originating from the process solutions increases with decreasing total sulphate

Fig. 5. Distribution coefficients of K^+, Fe^{2+}, and Fe^{3+} for $NH_4Al(SO_4)_2 \cdot 12H_2O$ crystallization plotted vs. the NH_4^+/Al^{3+} molar ratio in solution before crystallization (filled triangles: process solutions, open triangles: synthetic solutions).

Table 5
Solubilities of $CaSO_4 \cdot 2H_2O$ (expressed as Ca^{2+} concentrations) at 25 °C in mother liquors after crystallization of $NH_4Al(SO_4)_2 \cdot 12H_2O$ from process solutions

Experiment	Solution	NH_4^+/Al^{3+} molar ratio before crystallization	Concentration (g/kg solution)		
			SO_4^{2-} total	H_2SO_4	Ca^{2+}
7	G	0.34	153	40	0.35
8	G	0.34	151	40	0.33
11	H	0.49	138	35	0.42
14	I	0.74	113	25	0.55
15	I	0.74	110	25	0.53
16	I	0.74	117	25	0.54
17	J	0.99	86	14	0.61
18	J	0.99	87	14	0.60

Table 6
Average values of the distribution coefficients $D_{i,Al}$ for Cr^{3+}, Fe^{2+}, Fe^{3+}, Mg^{2+}, Na^+, and Zn^{2+} ions according to Eq. (6) in experiments with crystallization of $NH_4Al(SO_4)_2 \cdot 12H_2O$ from synthetic and process solutions (average value ± standard deviation; *n*: number of experimental values—Table 4)

	Distribution coefficient, $D_{i,Al}$				
	Cr^{3+}	Fe	Mg^{2+}	Na^+	Zn^{2+}
Synthetic solutions ($n = 6$)	0.27 ± 0.04	0.018 ± 0.004[a]	0.032 ± 0.010	0.067 ± 0.010	0.026 ± 0.005
Process solutions ($n = 8$)	0.20 ± 0.02	0.074 ± 0.030[b]	0.032 ± 0.004	0.085 ± 0.019	0.032 ± 0.007

[a] Fe^{2+}.
[b] Fe^{3+}.

concentrations in mother liquors. Since the total sulphate concentrations decrease with increasing yields of alum crystals, it can be stated that increasing the NH_4^+/Al^{3+} molar ratio in the solution before crystallization brings about not only the higher yields of alum crystals but also a lower tendency to $CaSO_4 \cdot 2H_2O$ scale formation (via increasing the $CaSO_4 \cdot 2H_2O$ solubility).

Even though data concerning solubility of $CaSO_4 \cdot 2H_2O$ in acidic $NH_4Al(SO_4)_2 \cdot 12H_2O$ solution are not available in the literature, from Fig. 6, it follows that the $CaSO_4 \cdot 2H_2O$ solubility in mother liquors exhibits a similar trend as the $CaSO_4 \cdot 2H_2O$ solubility in the sulphuric acid solution [16]. For the same total sulphate concentration, the solubility values in process solutions are lower than those in sulphuric acid solutions. This can be inter-

preted in such a way that in the latter, more acidic solutions, a larger proportion of SO_4^{2-} ions is converted into bisulphate ions [16], and due to the effect of the $CaSO_4 \cdot 2H_2O$ solubility product, the equilibrium value of the Ca^{2+} concentration increases.

4. Conclusions

In desalination of waste waters from the underground uranium leaching (exemplified by the concentrated process solutions from the Stráž pod Ralskem mining area), it is possible to increase the $NH_4Al(SO_4)_2 \cdot 12H_2O$ yield by a factor of at least 2.5 by addition of ammonium ions to the concentrated process solutions in such a way that the molar ratio NH_4^+/Al^{3+} in the solution before crystallization increases to the value of unity. The mass of ammonium ions in mother liquors will then still be lower than the mass of ammonium ion in the initial solution (before the addition of ammonium ions).

At low values of the NH_4^+/Al^{3+} molar ratio in solution, potassium ion (as an impurity which prevents the use of $NH_4Al(SO_4)_2 \cdot 12H_2O$ in some applications) is preferentially built into the alum crystals. By increasing the NH_4^+/Al^{3+} molar ratio, it is possible to decrease the uptake of potassium by a factor of about 3.5. As quantified by the values of the distribution coefficient $D_{i,Al}$, potassium ions exhibits the highest tendency to be incorporated into alum crystals, followed by Cr^{3+}, Na^+, Fe^{3+}, Mg^{2+}, Zn^{2+}, and Fe^{2+} ions.

Solubilities of $CaSO_4 \cdot 2H_2O$ in mother liquors after $NH_4Al(SO_4)_2 \cdot 12H_2O$ crystallization were determined at 25 °C. The $CaSO_4 \cdot 2H_2O$ solubility decreases with the increasing total sulphate concentrations. From the practical point of view, it is important that the solubility of $CaSO_4 \cdot 2H_2O$ has a high value (the tendency to $CaSO_4 \cdot 2H_2O$ scaling is low) under the same conditions as those which define the maximum crystal yield.
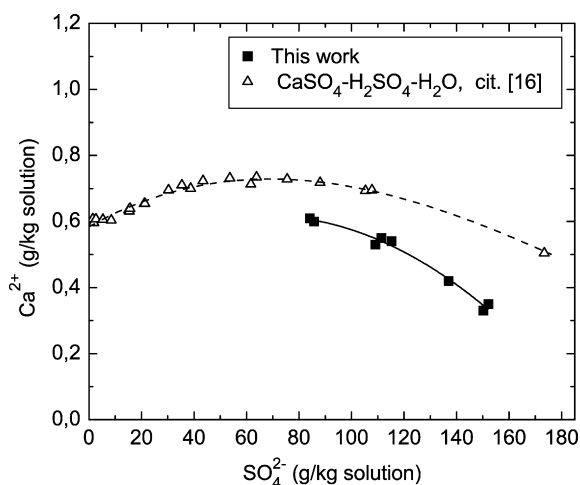

Fig. 6. Solubility of $CaSO_4 \cdot 2H_2O$ at 25 °C in mother liquors after crystallization of $NH_4Al(SO_4)_2 \cdot 12H_2O$ from process solutions vs. total sulphate concentration in these mother liquors. For comparison, solubility of $CaSO_4 \cdot 2H_2O$ in sulphuric acid at 25 °C [16] is also plotted.

Acknowledgements

References

[1] E. Jackson, Hydrometallurgical Extraction and Reclamation, Ellis Horwood, Chichester, UK, 1986, p. 55 and 61.

[2] J. Novák, Groundwater remediation in the Stráž leaching operation, Mine Water Environ. 20 (2001) 158–167.

[3] H.C. Park, Y.J. Park, R. Stevens, Synthesis of alumina from high purity alum derived from coal fly ash, Mater. Sci. Eng., A 367 (2004) 166–170.

[4] S.H. Lin, M.C. Lo, Recovery of aluminum alum from waste anode-oxidizing solution, Waste Manage. 18 (1998) 281–286.

[5] S.H. Lin, M.C. Lo, Synthesis of aluminum alum sulfate from waste aluminum processing solution by crystallization, J. Hazard. Mater. B 63 (1998) 211–222.

[6] M.A. Mohamed, M.E. Kassim, E.A. El-katatny, Optimization of the extraction of aluminum sulfate and ammonium aluminum sulfate alums from aluminum dress tailings, J. Mater. Res. 13 (1998) 1075–1083.

[7] Value improvements of clays, US Patent 6153157 (2000).

[8] Process for preparing low iron ammonium alum, US Patent 5470444 (1995).

[9] Method for obtaining analytical grade ammonium aluminium alum, Bulgarian Patent 46204 (1989).

[10] V. Hostomská, J. Hostomský, Solubility of ammonium aluminum sulfate dodecahydrate in the aluminum sulfate + ammonium sulfate + sulfuric acid + water system at (25,30,40 and 50) °C, J. Chem. Eng. Data 51 (2006) 243–247.

[11] Powder Diffraction File (PDF-2 Release 2004), International Centre for Diffraction Data, Newton Square, PA, 2004.

[12] G.G. Urazov, P.S. Kindyakov, Solubility study in the ternary system ammonium sulphate–aluminum suphate–water at 0, 25, 50, 75, and 90 °C, Trudy Mosk. Inst. Tonkoi Khim. Tekhnol. 7 (1958) 81–88.

[13] G.J. Witkamp, G.M. van Rosmalen, Growth of gypsum. II. Incorporation of cadmium, J. Cryst. Growth 108 (1991) 89–98.

[14] G.I. Gorshtein, Trudy IREA, No. 20 (1951), p. 3 (cited according to I.V. Melikhov, M.S. Merkulova, Co-crystallization (in Russian), Khimia, Moscow, USSR, 1975, p. 195).

[15] A.E. Hill, N. Kaplan, Ternary systems. XXII. Formation of solid solutions from alums, J. Am. Chem. Soc. 60 (1938) 550–554.

[16] W.L. Marshall, E.V. Jones, Second dissociation constant of sulfuric acid from 25 to 350° evaluated from solubilities of calcium sulfate in sulfuric acid solutions, J. Phys. Chem. 70 (1966) 4028–4040.