



Separation of critical radioactive and non-radioactive species from aqueous waste streams

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Abstract

The separation of radioactive and non-radioactive species from the simulated DOE neutralized current acid waste (NCAW) stream was studied. Cation and anion species were referred to their possible basic compounds, and divided into seven groups (nitrate, phosphate, sulfate, fluoride, nitrite, carbonate, and hydroxide). The nitrate group (the major anion in the DOE waste streams) contains several cations species, while the rest of the groups are only in the form of sodium. The precipitation measurements were conducted in three experimental stages. In the first stage, the precipitation of sodium sulfate, sodium phosphate, sodium-sulfate-phosphate, and aluminum nitrate systems were studied using isopropylamine (IPA) as a precipitation solvent. The objectives of this stage were to evaluate the precipitation ability of IPA in precipitating these compounds individually, and to validate the consistency of the analytical instruments and the employed experimental procedure. Tests performed on the acquired data indicated a high level of experimental consistency. The removal of phosphate, sulfate and aluminum were very high. In the second stage, the precipitation studies were conducted on the: (1) nitrate group alone; (2) binary groups containing the groups of nitrate–phosphate, nitrate–sulfate, nitrate–fluoride, nitrate–nitrite, and nitrate–carbonate; (3) combined nitrate, phosphate, sulfate, and fluoride groups and (4) combined nitrate, phosphate, sulfate, fluoride, nitrite, and carbonate groups. IPA was used as a precipitation solvent. The objectives of this stage were to evaluate the interactions of these groups in the absence of the hydroxide group (e.g. DOE acid-dissolved sludge and acidified supernate streams), and the influence of such interactions on the individual removal of the targeted species. The removal of the aluminum, phosphate, fluoride, and alkaline cations were significantly high (reached 99.9%). The removal of sulfate were moderately high (reached 87%), and the removal of nitrate and alkali cations including cesium were to some extent low (reached about 50%).

In the third stage, the precipitation of inorganic species from the simulated NCAW stream was studied using IPA and ethylamine (EA). The precipitation process is very feasible for reducing the radioactivity contents of alkaline cations. However, the process is less effective in separating

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alkali cations including cesium. The removal of polyvalent transition metals such as aluminum ion is negatively influenced by the significant presence of hydroxide. While the process is effectively capable of separating phosphate, fluoride, and sulfate, it is significantly less effective in separating nitrate and nitrite. A previously derived thermodynamics framework was used to model the precipitation measurements. The framework provided two predictive equations (the 2-Suffix and 3-Suffix equations). Both equations were reasonably adequate for predicting the solubility phase behavior of tested inorganic species in a mixed-solvents mixture as well as for estimating optimum interaction parameters. However, the 3-Suffix equation was better than the 2-Suffix equation. The parameters were useful for estimating the: (1) precipitation fractions (%*P*) of the studied species, for instance, at different concentration levels of similar targeted species, or in different waste streams with similar or approximate abundance of species, or at different solvents volume ratio (V_r) where no experimental data are available. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Over the past 50 years, about 100 million gal of high-level waste (HLW), 50 million gal of transuranic waste, 870 million gal of low-level waste (LLW), and 38.5 million gal of mixed low-level waste were generated as a result of nuclear weapons production [1]. About 335 underground tanks were used to process and store radioactive wastes. The stored wastes are in forms of sludge, slurry, and supernate.

Most of the DOE storage tanks contain waste with a diverse portfolio of inorganic anions (hydroxide, nitrate, nitrite, carbonate, sulfate, phosphate, and fluoride) mainly in form of sodium. Temperature profiles of these tanks vary from near ambient to temperatures over 93°C [2]. Much of the radioactivity and heat arises from cesium, strontium, and to a lesser extent from technetium and actinides. Cesium is the primary radioactive component found in supernatants [2,3]. Strontium and technetium tend to be concentrated in sludge washing liquids while actinides tend to be concentrated in the sludge portion [2,3].

Environmental restoration of such wastes has become one of the primary missions of the DOE. The DOE strategy is centered on expending separation methods to pretreat radioactive wastes. Pretreatment methods involve three steps: (1) separation of the waste into liquid and solid portions; (2) reduction of radioactive content of the liquid portion and (3) removal of non-radioactive species from the solid portion. These methods provide a sequence of processes to partition the waste mainly into a small volume of HLW for deep geologic disposal and a larger volume of LLW for burial in near-surface facilities.

Vitrification, the process of converting materials into a glass-like substance, is the preferred immobilization method. However, the estimated cost of vitrification and repository is about \$1 million per glass canister (1650 kg) [2]. For instance, about 200,000 canisters would be required at the Hanford site, if the wastes were not treated [4]. As such, pretreatment technologies for selective removal of targeted radioactive and non-radioactive species from the high-activity liquid and solid portions are vigorously pursued to reduce the cost of vitrification.

Certain liquid waste streams require removal of cesium, strontium, technetium, and actinides. Several promising technologies such as solvent extraction, pressure-driven

Nomenclature

%AAD	percent average absolute deviation
$C_{1,m}$	concentration of salt species in filtered sample
$C_{1,2}$	concentration of salt species in standard sample
C_i	model's interaction parameters
NP	number of points
P	precipitation fraction
RMSE	root mean square error
SS	objective function
v_i	molar volume of solvent i
V_i	volume of solvent i
V_r	solvents volume ratio (organic/water)
$x_{i,j}$	mole fraction (solubility) of species i in solvent j
$x_{i,m}$	mole fraction (solubility) of species i in mixed-solvents mixture m

Greek symbols

Δ_1	the salt binary-solvent interaction parameter (ternary constant)
Δ_{ij}	interaction parameter of solvent i with solvent j
θ_i	volume fraction of solvent i
σ	standard deviation

Subscripts

1	salt species
2	water solvent
3	organic solvent
Cal	calculated
Exp	experimental
m	mixed-solvent mixture

Superscripts

E	excess
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membranes, and ion exchangers are rigorously pursued. Solvent extraction has gained significant consideration for the DOE applications in separation of radioactive alkali and alkaline cations from liquid streams (see [5–7]). Factors such as ion speciation in strong mixed-cation mixtures and sensitivity to the volume (capacity) and grade (solid-free) of the liquid stream are yet to be resolved.

Pressure-driven membrane processes (nanofiltration, ultrafiltration, and microfiltration) enhanced with molecular recognition agents attached to flow-through membranes have been tested for selective removal of strontium, cesium, and technetium from aqueous streams (see [8–10]). Factors such as membrane stability (e.g. concentration polarization, membrane fouling, osmotic pressure, pH limits), separation selectivity, and capacity are critical issues that are under evaluation.

Table 1
A simulant profile for the neutralized current acid waste (NCAW) stream [11]

Species	Concentration (ppm)	Compound	Concentration (ppm)
Cations			
		Group 1 — nitrate	
Na	114700.00	Al(NO ₃) ₃ ·9H ₂ O	161310.20
K	4692.00	NaNO ₃	21965.70
Rb	4.27	KNO ₃	12132.00
Cs	66.45	RbNO ₃	7.38
Mg	0.00	CsNO ₃	97.50
Ca	0.00	Ca(NO ₃) ₂ ·4H ₂ O	0.00
Sr	0.00	Sr(NO ₃) ₂	0.00
Ba	0.00	Group 2 — phosphate	
Al	11602.06	Na ₃ PO ₄ ·12H ₂ O	9502.50
		Group 3 — sulfate	
		Na ₂ SO ₄	21300.00
Anions			
F	1690.00	Group 4 — fluoride	
NO ₃	103486.18	NaF	3738.00
NO ₂	19782.37	Group 5 — nitrite	
PO ₄	2374.28	NaNO ₂	29670.00
SO ₄	14408.64	Group 6 — carbonate	
CO ₃	13802.12	Na ₂ CO ₃	24380.00
OH	57824.96	Group 7 — hydroxide	
		NaOH	136000.00

Ion exchangers are currently under development for the removal of cesium and strontium from concentrated and diluted aqueous streams (see [11–13]). Organic and inorganic exchange materials are employed in the ion exchange process. Although both exchange materials exhibit strong retention for cesium and strontium, factors such as chemical stability, capacity, reversibility of exchange, and vitrification of used resins (cesium volatilizes in the melter and leads to a highly radioactive off-gas problem) are the basic limitations.

Table 2
Precipitation measurements for sodium sulfate system using IPA

V_r^a	%P/ σ_P	
	SO ₄	Na
1.0	57.6	57.6
	3.3E–1	2.9E0
1.4	79.8	80.8
	5.1E–1	5.3E–1
2.0	95.3	95.0
	3.6E–2	4.0E–1
$C_{1,2}^b$	14408.3	6896.8
$C_{1,2}^c$	14348.6	7084.9
$\sigma_{C_{1,2}}$	132.5	196.2

^a Ratio of the organic solvent volume (IPA) to the aqueous volume.

^b Weighed concentration of each ion in de-ionized water (ppm).

^c Determined concentration of each ion in de-ionized water by IC (ppm).

Table 3
Precipitation fractions for sodium phosphate system using IPA

V_r^a	%P/ σ_P	
	PO ₄	Na
0.8	74.0	69.4
	1.3E0	1.4
1.0	88.2	84.4
	5.8E-1	7.1E-1
1.4	97.2	94.8
	1.4E0	3.9E-1
2.0	99.9	98.5
	2.9E-3	9.1E-2
$C_{1,2}^b$	2373.4	1723.6
$C_{1,2}^c$	2348.3	1727.8
$\sigma_{C_{1,2}}$	28.4	51.3

^a Ratio of the organic solvent volume (IPA) to the aqueous volume.

^b Weighed concentration of each ion in de-ionized water (ppm).

^c Determined concentration of each ion in de-ionized water by IC (ppm).

The bulk of the radioactivity is known to be in the sludge portion which makes it the largest source of HLW. Removal of key non-radioactive species such as aluminum, sulfate, phosphate, nitrate, fluoride, and in some case chromate salts from the sludge portion is very critical to reduce the volume of HLW and prevent operation problems during vitrification. Aluminum is present in very large quantities in most tank wastes (3.5×10^6 kg in the Hanford tanks [3]). Most, if not all wastes, are significantly rich in nitrate salts, and to a much lesser extent in sulfate, phosphate, and fluoride salts. The presence of these species in even

Table 4
Precipitation measurements for sodium-phosphate-sulfate system using IPA

V_r^a	%P/ σ_P		
	PO ₄	SO ₄	Na
0.6	89.9	30.8	42.2
	9.1E-2	3.4E0	6.5E-1
0.8	97.8	39.0	52.1
	1.9E-2	3.0E0	5.7E-1
1.0	99.3	68.1	73.6
	5.7E-3	1.6E0	4.4E-1
1.4	>99.9	91.7	92.3
		4.2E-1	2.2E-1
2.0	>99.9	98.4	97.5
		8.0E-2	2.4E-1
$C_{1,2}^b$	2374.5	14410.3	8622.2
$C_{1,2}^c$	2373.6	14434.2	8702.7
$\sigma_{C_{1,2}}$	11.0	715.2	177.3

^a Ratio of the organic solvent volume (IPA) to the aqueous volume.

^b Weighed concentration of each ion in de-ionized water (ppm).

^c Determined concentration of each ion in de-ionized water by IC (ppm).

Table 5
Precipitation measurements for aluminum nitrate system using IPA

V_r^a	%P/σ P	
	NO ₃	Al
0.025	8.1	41.9
	3.1E0	2.5E0
0.050	11.0	63.2
	3.2E0	1.9E0
0.1000	18.4	97.7
	2.8E0	5.1E-2
0.200	21.7	>99.9
	2.7E0	
0.400	33.2	>99.9
	2.4E0	
0.600	38.8	>99.9
	2.1E0	
0.800	44.1	>99.9
	2.0E0	
1.000	96.5	>99.9
	1.2E0	
$C_{1,2}^b$	79985.7	11602.0
$C_{1,2}^c$	81103.2	11651.6
$\sigma_{C_{1,2}}$	2780.9	190.2

^a Ratio of the organic solvent volume (IPA) to the aqueous volume.

^b Weighed concentration of each ion in de-ionized water (ppm).

^c Determined concentration of each ion in de-ionized water by IC (ppm).

low concentrations can cause serious problems during vitrification. These non-radioactive species tend to form low-temperature eutectics in the melter cold caps and segregate from the remaining feed components at concentrations well below their solubility limits in the glass. Once segregated, nitrate salts tend to decompose to gaseous species, while the remaining sulfate, phosphate, and chromate salts tend to aggressively attack refractories at the melt line [14]. Thus, such species pose safety risks and diminish the efficiency of vitrification. For instance, feeding the melter with liquid slurry leads to possible steam explosion, and to avoid this situation, the vitrification plant will run at a lower waste loading. On the other hand, fluoride and possibly other halides such as chloride reduce the melt viscosity (e.g. 1 mass percent of fluoride added to a typical waste glass can reduce the melt viscosity by more than 6 P) [14].

Sludge pretreatment with caustic solutions is aimed at removing some of such critical non-radioactive species. Dilute hydroxide washing is the minimum pretreatment for some of the tank sludge [2]. The sludge is mixed with 0.1 M solution of sodium hydroxide followed by a solid-liquid separation. The fundamental aims of the process are to [15]: (1) remove aluminum by converting aluminum oxides/hydroxides to sodium aluminate and (2) remove a portion of phosphate and sulfate by metathesizing water-insoluble metal phosphates and sulfates to insoluble hydroxides and soluble sodium phosphate and sodium sulfate. The process, however, is ineffective in removing such key non-radioactive species [2].

Table 6
Precipitation measurements for group 1 (nitrate) of the NCAW stream using IPA

V_r^a	%P/ σ_P						
	Al	NO ₃	Na	K	Cs	Ca	Sr
0.025	35.6	4.7	1.0	2.9	n.a. ^b	9.8	20.7
	1.1E0	1.1E0	8.5E-1	1.0E0		1.2E0	5.4E-1
0.050	59.1	7.4	6.1	4.0	n.a.	n.a.	21.8
	1.2E0	1.1E0	8.1E-1	1.0E0			5.4E-1
0.100	>99.9	10.9	n.a.	5.3	20.8	n.a.	44.6
		1.1E0		1.0E0	6.0E-1		
0.200	99.9	17.4	21.1	8.6	34.5	94.2	5.1E-1
	1.3E-2	1.0E0	7.3E-1	1.0E0	5.0E-1	7.4E-2	1.0E-2
0.400	99.8	24.7	31.0	24.1	38.2	97.5	>99.9
	1.2E-3	8.9E-1	6.1E-1	8.8E-1	4.7E-1	3.2E-2	
0.600	99.9	33.6	38.9	29.1	n.a.	97.6	>99.9
	1.8E-4	8.4E-1	5.4E-1	7.9E-1		3.1E-2	
0.800	99.9	42.1	47.0	34.8	46.6	>99.9	>99.9
	3.1E-3	7.2E-1	4.8E-1	7.3E-1	4.0E-1		
1.000	>99.9	48.3	50.4	41.5	57.0	>99.9	>99.9
		6.2E-1	4.3E-1	7.4E-1	3.3E-1		
$C_{1,2}^c$	11602.1	104029.3	5941.7	4692.0	101.9	100.3	102.3
$C_{1,2}^d$	11602.6	104227.2	6086.0	4691.3	107.0	97.7	98.6
$\sigma_{C_{1,2}}$	53.2	959.5	147.3	35.2	1.4	3.7	2.6

^a Ratio of the organic solvent volume (IPA) to the aqueous volume.

^b Not available.

^c Weighed concentration of each ion in de-ionized water (ppm).

^d Determined concentration of each ion in de-ionized water by IC (ppm).

Enhanced sludge washing (ESW) is the baseline sludge pretreatment method [2]. The ESW method involves first the addition of 3 M of sodium hydroxide to dissolve aluminum. The sludge is then washed with an aqueous solution containing dilute sodium hydroxide and sodium nitrate to remove interstitial liquid and any remaining soluble solids [2]. Two problems are encountered with the use of the ESW method. First, inadequate removal of key non-radioactive species always result in production of an unacceptably large volume of HLW. It is estimated that 14,600 m³ of immobilized HLW will be produced in processing, for instance, Hanford tanks sludge if the ESW method is implemented [16]. Second, the caustic and washing steps in sludge retrieval and pretreatment use large volumes of sodium hydroxide, sodium nitrate, and sodium nitrite, which add an additional 25% of sodium to the volume of wastes that need to be treated. This also generates excessive amounts of aqueous solutions which require a treatment as secondary wastes. Minimizing, if not eliminating, the amount of caustic and wash solutions to cut the volumes of both HLW and LLW is a must. This can be accomplished by combining effective advanced separation processes either with carefully optimized ESW method (caustic-dissolved sludge), or with acid-dissolved sludge methods to reduce the immobilized HLW, as suggested [17], by at least a factor of 10.

Obviously, alternative technologies are needed to treat radioactive aqueous streams, and to supplement the toolbox of the DOE under development technologies. As such, we have proposed a novel simple process (see [18–21]) that consists of three steps: precipitation,

Table 7

Precipitation measurements for groups 1 (nitrate) and 2 (phosphate) of the NCAW stream using IPA

V_r^a	%P/ σ_p						
	Al	PO ₄	NO ₃	Na	K	Cs	Sr
0.1	99.9	95.4	9.5	1.8	2.4	17.0	49.6
	1.0E-2	2.9E-2	1.0E0	8.3E-1	9.2E-1	6.3E-1	1.2E0
0.2	99.9	97.3	12.0	14.8	6.3	20.5	90.1
	7.3E-3	1.7E-2	9.8E-1	7.2E-1	8.9E-1	6.0E-1	5.5E-1
0.4	99.9	97.7	17.0	20.5	16.8	50.2	95.2
	8.5E-3	1.4E-2	9.3E-1	6.7E-1	7.9E-1	3.8E-1	1.0E-1
0.6	99.9	98.5	19.9	25.9	n.a. ^b	53.0	>99.9
	6.9E-3	9.2E-3	8.9E-1	6.2E-1		3.6E-1	
0.8	>99.9	98.9	41.5	45.8	36.9	n.a.	>99.9
	1.6E-3	7.0E-3	6.5E-1	4.6E-1	6.0E-1		
1.0	>99.9	99.3	45.7	53.8	41.8	n.a.	>99.9
		4.6E-3	6.1E-1	3.9E-1	5.5E-1		
1.4	>99.9	>99.9	56.0	61.8	45.4	56.9	>99.9
			4.9E-1	3.2E-1	5.2E-1	3.3E-1	
2.0	>99.9	>99.9	63.7	68.3	56.6	n.a.	>99.9
			4.2E-1	2.7E-1	4.1E-1		
$C_{1,2}^c$	11602.4	2374.3	103720.0	7666.9	4692.0	100.2	100.2
$C_{1,2}^d$	11888.3	2373.6	103569.3	7731.0	4691.8	104.0	100.0
$\sigma_{C_{1,2}}$	545.6	10.6	817.7	66.1	31.4	1.4	2.6

^a Ratio of the organic solvent volume (IPA) to the aqueous volume.^b Not available.^c Weighed concentration of each ion in de-ionized water (ppm).^d Determined concentration of each ion in de-ionized water by IC (ppm).

filtration-clarification, and reuse of the precipitation agent. Precipitation is the first step in which a suitable organic solvent will be added to a targeted aqueous stream to form selective precipitates. In the second step, the formed selective precipitates will be filtered from the aqueous stream. The solvent will then be recovered and recycled in the third step.

The objectives of this work were to: (1) demonstrate the technical feasibility of the proposed process for the separation of radioactive species as well as key non-radioactive species from concentrated (NCAW) DOE aqueous streams and provide basic performance data employing bench-scale process testing and (2) evaluate our developed solubility (solid–liquid equilibrium, SLE) framework equations in correlating the acquired precipitation data, estimating the solubilities of the tested inorganic species in the organic solvent, and providing optimum interaction parameters.

2. The proposed precipitation concept

The selection of an organic solvent is the most significant aspect in the precipitation process. The suitable solvents are those which have the capability to meet two basic criteria: (1) suitability to precipitate targeted inorganic species from aqueous solutions and (2) suitability for overall process design.

Table 8
Precipitation measurements for groups 1 (nitrate) and 3 (sulfate) of the NCAW stream using IPA

V_r^a	%P/ σ_P							
	Al	SO ₄	NO ₃	Na	K	Cs	Ca	Sr
0.025	30.8	28.7	3.6	6.6	5.6	8.2	36.0	63.8
	5.8E0	4.4E-1	1.1E0	7.9E-1	9.0E-1	1.6E0	8.2E-1	2.5E-1
0.050	61.7	55.6	8.3	8.0	6.3	n.a. ^b	53.3	73.6
	3.9E0	2.8E-1	1.0E0	7.8E-1	8.9E-1		6.0E-1	1.8E-1
0.100	>99.9	54.0	9.3	10.5	13.2	31.9	n.a.	76.4
		3.3E-1	1.1E0	7.5E-1	8.2E-1	5.1E-1		1.6E-1
0.200	99.9	20.8	14.4	15.7	15.2	46.5	92.3	96.6
	1.1E-2	4.9E-1	1.2E0	7.1E-1	8.0E-1	4.0E-1	9.9E-2	2.3E-2
0.400	99.9	21.8	14.5	21.1	16.0	n.a.	92.3	99.0
	7.1E-3	6.2E-1	9.5E-1	6.7E-1	7.9E-1		9.9E-2	6.4E-2
0.600	99.9	29.0	16.0	25.3	17.4	n.a.	94.9	>99.9
	4.9E-3	5.9E-1	9.4E-1	6.3E-1	7.8E-1		3.0E-2	
0.800	99.9	42.7	22.2	30.5	18.0	n.a.	95.2	>99.9
	4.0E-3	3.6E-1	9.0E-1	6.9E-1	7.8E-1		6.2E-2	
1.000	>99.9	57.9	24.1	37.5	45.9	61.2	95.6	>99.9
	1.4E-3	2.6E-1	8.7E-1	5.3E-1	5.1E-1	2.9E-1	2.3E-1	
$C_{1,2}^c$	11602.4	14412.4	104026.3	12839.6	4691.0	101.3	99.6	103.1
$C_{1,2}^d$	11813.9	14408.1	103595.1	12856.8	4692.1	120.8	100.1	100.0
$\sigma_{C_{1,2}}$	669.9	63.6	817.9	76.7	33.9	1.6	0.9	1.4

^a Ratio of the organic solvent volume (IPA) to the aqueous volume.

^b Not available.

^c Weighed concentration of each ion in de-ionized water (ppm).

^d Determined concentration of each ion in de-ionized water by IC (ppm).

The selected organic solvent must be miscible with the aqueous phase. Of equal importance, targeted inorganic salts must be sparingly soluble (preferably insoluble) in the organic solvent. The addition of such a solvent to an inorganic-aqueous solution leads to capture of part of the water molecules and reduces the solubility of inorganic in water which forms insoluble precipitates. The nature of the influence of the organic solvent on the hydration of inorganic needs to be assessed. Such an influence can be determined by studying the solubility of inorganic in mixed-solvents media (water and organic). Solubility is thus the obvious thermodynamic property of concern in forming and affecting salt precipitates.

The practicality of the precipitation process depends on the capability of effectively recovering and recycling the precipitation agent. For ease of recovery and recycle, the selected organic solvent must have favorable physical properties such as low boiling point, high vapor pressure, high relative volatility, and no azeotrope formation with water. From a process design standpoint, the selected organic solvent must have low toxicity since traces of the organic solvent (ppm–ppb levels) always remain in the discharge stream. The solvent vapors are also of prime health and environmental concerns. Furthermore, the selected organic solvent must be chemically stable, compatible with the process, and relatively inexpensive. These characteristics are very important because of their economic and environmental impacts on the overall process design.

Table 9

Precipitation measurements for groups 1 (nitrate) and 4 (fluoride) of the NCAW stream using IPA

V_r^a	%P/ σ_P						
	Al	F	NO ₃	Na	K	Cs	Sr
0.025	56.6	98.5	9.1	2.9	1.1	7.4	56.2
	1.8E0	1.5E-1	2.9E0	8.2E-1	9.4E-1	7.5E-1	3.0E-1
0.050	80.6	98.6	9.7	3.2	3.2	9.0	58.8
	8.9E-1	1.4E-1	2.9E0	8.2E-1	9.2E-1	6.9E-1	2.8E-1
0.100	>99.9	98.8	9.9	4.4	3.7	14.9	65.3
		1.1E-1	2.8E0	8.1E-1	9.1E-1	6.4E-1	5.5E-1
0.400	>99.9	75.9	28.7	31.0	22.3	40.7	>99.9
		2.3E0	2.3E0	5.8E-1	7.4E-1	4.5E-1	
0.600	>99.9	80.6	34.3	37.1	27.0	60.6	>99.9
	4.9E-3	1.9E0	2.1E0	5.3E-1	6.9E-1	3.0E-1	
0.800	>99.9	83.9	35.6	39.5	27.4	68.8	>99.9
	1.1E-3	1.6E0	2.1E0	5.1E-1	6.9E-1	2.4E-1	
1.000	>99.9	87.2	35.2	43.4	31.1	80.7	>99.9
		1.2E0	2.0E0	4.7E-1	6.5E-1	1.5E-1	
$C_{1,2}^b$	11602.3	1692.4	103721.2	7989.9	4694.9	102.0	99.9
$C_{1,2}^c$	11602.6	1800.2	104937.5	8020.4	4853.2	106.7	100.0
$\sigma_{C_{1,2}}$	53.2	174.1	1568.7	52.6	169.1	1.8	0.5

^a Ratio of the organic solvent volume (IPA) to the aqueous volume.^b Weighed concentration of each ion in de-ionized water (ppm).^c Determined concentration of each ion in de-ionized water by IC (ppm).

The presence of a “suitable anion” in a targeted inorganic-aqueous mixture plays an important role in affecting and characterizing the precipitation step. The role of such an “anion” can be seen in controlling the rate of change in the pH values, and in forming a basic salt which, by precipitation, reduces the cation concentration.

In our preliminary work, several organic solvents have been identified for potential use in the proposed process [18,19]. The identified solvents are amines selected from a group which includes isopropylamine (IPA), ethylamine (EA), propylamine (PA), diisopropylamine (DIPA), diethylamine (DEA), and dimethylamine (DMA). However, IPA and EA are the preferred precipitation solvents. The preference of IPA and EA is attributed to their: (1) precipitation capability with several salts including sulfate and chloride in the forms of monovalent and divalent cations [19–23]; (2) favorable physical properties (bp: 32.4°C for IPA and 16.6°C for EA; vapor pressure: 478 mmHg at 20°C for IPA and 760 mmHg at 16.6°C for EA) and (3) minimal environmental risks. IPA salts, for instance, have been used as a herbicide for agricultural purposes [23]. Vapor–liquid equilibrium calculations indicate that 99.9% recovery of IPA or EA from the aqueous phase can possibly be achieved by a vacuum system [23].

The amount of experimental precipitation data required can be reduced when a practical model with minimum empiricism and reliable predictive capabilities is developed. However, the physical chemistry of inorganic-aqueous systems is complex due to phenomenon of interactions such as long-range electrostatic interactions between ions, solvation of ions, and the association between cations and anions. These interactions become more

Table 10
Precipitation measurements for groups 1 (nitrate) and 5 (nitrite) of the NCAW stream using IPA^a

V_r^b	%P/ σ_P					
	Al	NO ₃	Na	K	Cs	Sr
0.025	39.2	1.2	3.0	1.3	9.6	62.2
	2.9E0	1.1E0	8.2E-1	9.3E-1	6.8E-1	2.6E-1
0.050	65.5	3.1	3.8	4.0	12.6	63.1
	1.5E0	1.1E0	8.1E-1	9.1E-1	4.6E-1	2.5E-1
0.100	>99.9	6.9	4.9	5.3	14.5	93.6
		1.0E0	8.0E-1	9.0E-1	6.5E-1	4.4E-2
0.200	99.7	13.0	12.5	7.2	n.a. ^c	>99.9
	1.6E-2	9.7E-1	7.4E-1	8.8E-1		
0.400	99.9	24.0	13.6	10.6	29.8	>99.9
	7.4E-3	8.5E-1	7.4E-1	8.5E-1	1.5E-1	
0.600	99.9	29.6	20.1	16.4	n.a.	>99.9
	7.3E-3	7.9E-1	6.7E-1	7.9E-1		
0.800	99.9	31.5	21.5	18.0	n.a.	>99.9
	1.0E-2	7.6E-1	6.6E-1	7.8E-1		
1.000	>99.9	42.3	33.3	28.1	n.a.	>99.9
	1.7E-3	6.4E-1	5.6E-1	6.8E-1		
$C_{1,2}^d$	11602.4	103721.1	15827.1	4692.8	101.9	101.6
$C_{1,2}^e$	11602.6	120478.9	15846.7	4691.1	105.7	100.0
$\sigma_{C_{1,2}}$	53.2	1705.4	94.5	30.3	1.4	0.6

^a NO₂ is converted into NO₃ and NO₂ (gas).

^b Ratio of the organic solvent volume (IPA) to the aqueous volume.

^c Not available.

^d Weighed concentration of each ion in de-ionized water (ppm).

^e Determined concentration of each ion in de-ionized water by IC (ppm).

complicated for systems containing inorganic species in mixed-solvent (water–organic) mixtures.

Several theories have been proposed to describe the phase behavior of inorganic species in mixed-solvent mixtures [24]. A sensitive test for the abilities of a given theory is its usefulness in understanding the effect of various forces and interactions on thermodynamic properties (e.g. solubility, activity coefficient, and relative volatility). Yet, no theoretical treatment exists to fulfill such a purpose [23].

Semi-empirical models with fundamental foundation would provide reasonable approximation in targeted applications. As such, a framework derived from basic thermodynamic principles of solid–liquid equilibrium (SLE) criteria was developed to correlate the precipitation of salts from aqueous solutions using organic solvents [23,25]. The solubility (in terms of activity coefficient) of a given salt in a mixed-solvent mixture was related to solubilities (in terms of activity coefficients) of such a salt in each of the pure solvents (water and organic) using the excess Henry's constant approach [26]. The Wohl's expansion was then employed to model the excess Gibbs free energy (g^E) function [27]. Two equations were provided; the 2-Suffix equation (two parameters: $x_{1,3}$ and Λ_{32}) [25]

$$\ln(1 - P) = \ln\left(\frac{x_{1,m}}{x_{1,2}}\right) = \theta_3 \ln\left(\frac{x_{1,3}}{x_{1,2}}\right) + \theta_2 \theta_3 \frac{v_1}{v_3} \Lambda_{32} \quad (1)$$

Table 11
Precipitation measurements for groups 1 (nitrate) and 6 (carbonate) of the NCAW stream using IPA^a

V_r^b	%P/ σ_P					
	Al	NO ₃	Na	K	Cs	Sr
0.025	76.8	7.0	2.0	2.5	12.6	47.0
	5.4E-1	1.1E0	8.3E-1	9.3E-1	6.6E-1	3.6E-1
0.050	96.6	7.1	2.7	2.8	24.2	54.1
	4.6E-1	1.1E0	8.2E-1	9.3E-1	5.7E-1	3.1E-1
0.100	>99.9	9.0	9.1	4.8	24.8	99.2
		1.1E0	7.7E-1	9.1E-1	5.7E-1	5.4-3
0.200	99.9	19.4	14.6	8.6	n.a. ^c	>99.9
	2.5E-3	9.6E-1	7.2E-1	8.8E-1		
0.600	99.9	29.7	23.3	16.5	40.6	>99.9
	3.0E-3	8.4E-1	6.5E-1	8.0E-1	4.5E-1	
0.800	99.9	32.2	24.5	16.9	43.2	>99.9
	5.3E-3	8.1E-1	6.4E-1	8.0E-1	4.3E-1	
1.000	>99.9	41.3	34.4	24.7	n.a.	>99.9
		7.0E-1	5.5E-1	7.2E-1		
$C_{1,2}^d$	11602.2	103719.2	16517.7	4694.7	100.2	100.2
$C_{1,2}^e$	11691.3	104887.0	16615.5	4812.5	118.6	99.2
$\sigma_{C_{1,2}}$	53.2	1550.1	105.0	133.1	1.6	0.9

^a CO₃ is not determined.

^b Ratio of the organic solvent volume (IPA) to the aqueous volume.

^c Not available.

^d Weighed concentration of each ion in de-ionized water (ppm).

^e Determined concentration of each ion in de-ionized water by IC (ppm).

and the 3-Suffix equation (four parameters: $x_{1,3}$, Λ_{32} , Λ_{23} , and Λ_1) [25]

$$\ln(1 - P) = \ln\left(\frac{x_{1,m}}{x_{1,2}}\right) = \theta_3 \ln\left(\frac{x_{1,3}}{x_{1,2}}\right) - \theta_2 \theta_3 (2\theta_3 - 1) \Lambda_{32} \frac{v_1}{v_3} + 2\theta_2 \theta_3^2 \Lambda_{23} \frac{v_1}{v_2} + \Lambda_1 \theta_2 \theta_3 \quad (2)$$

where P is the precipitation fraction, $x_{1,2}$ the solubility of a given salt in water solvent, $x_{1,3}$ solubility of a given salt in organic solvent, $x_{1,m}$ solubility of a given salt in the mixed solvents (water-organic), θ_3 the salt-free volume fraction of organic solvent, θ_2 the salt-free volume fraction of water solvent, v_i the molar volume of species i (1: salt; 2: water; 3: organic solvent), Λ_{32} and Λ_{23} are solvent-solvent interaction parameters, and Λ_1 the salt binary-solvent interaction parameter (ternary constant). The P values of sulfate ion (14,410 ppm) and sodium ion (6897 ppm) from sodium sulfate system were identical and between 58.3% at a V_r of 1.0 and 95.6% at a V_r of 2.0. However, no precipitation was observed for sodium sulfate below a V_r of 1.0. Table 3 and Fig. 3

The approach followed in deriving Eqs. (1) and (2) was to transcend the complexity of inorganic interactions (ion-ion and ion-solvent interactions) by treating a system of given inorganic in a mixed-solvent mixture (water and organic) as a ternary system (inorganic-aqueous-organic) with explicit account for the solvent-solvent (aqueous-organic) interactions. Detailed derivation of the model equations is given elsewhere [25].

Table 12
Precipitation measurements for groups 1, 2, 3 and 4 (nitrate, phosphate, sulfate and fluoride) of the NCAW stream using IPA

V_r^a	%P/ σ_p									
	Al	PO ₄	F	SO ₄	NO ₃	Na	K	Cs	Ca	Sr
0.025	78.7 5.3E-1	>99.9	97.9 4.6E-1	55.2 2.8E-1	3.7 1.1E0	3.4 8.1E-1	2.7 9.2E-1	9.8 6.8E-1	31.6 1.9E0	34.7 4.5E-1
0.050	80.2 1.4E-1	>99.9	98.3 3.6E-2	54.8 8.6E-1	5.7 1.3E0	7.9 7.8E-1	8.9 8.6E-1	n.a. ^b	n.a.	45.8 1.6E0
0.100	>99.9 1.6E-3	>99.9	98.0 1.2E-2	20.0 5.0E-1	9.4 1.0E0	12.4 7.4E-1	14.5 8.1E-1	21.1 6.0E-1	92.3 1.5E-1	98.6 1.7E-1
0.200	98.4 1.3E-2	>99.9	80.1 1.2E-1	16.7 5.2E-1	14.4 9.6E-1	23.1 6.5E-1	16.4 7.9E-1	38.3 4.7E-1	95.1 6.2E-2	>99.9
0.400	99.3 2.2E-2	>99.9	80.6 1.2E-1	34.9 4.1E-1	28.1 8.0E-1	37.3 5.3E-1	28.0 6.8E-1	n.a.	97.4 3.3E-2	>99.9
0.600	99.5 4.6E-3	>99.9	86.2 8.5E-2	43.0 3.6E-1	33.0 7.5E-1	44.3 4.7E-1	30.7 6.6E-1	n.a.	99.0 1.3E-2	>99.9
0.800	99.7 3.5E-2	>99.9	90.7 5.7E-2	59.6 2.5E-1	40.7 6.6E-1	54.6 3.8E-1	33.7 6.3E-1	46.7 4.0E-1	99.1 1.2E-2	>99.9
1.000	99.8 1.3E-2	>99.9	90.2 6.0E-2	72.0 1.8E-1	47.0 5.9E-1	61.1 3.3E-1	43.1 5.4E-1	52.6 3.6E-1	99.4 7.8E-3	>99.9
$C_{1,2}^c$	11602.3	2375.2	1691.3	14407.6	104331.5	16610.7	4692.2	100.2	100.5	101.6
$C_{1,2}^d$	11612.6	2375.2	1690.5	14488.8	103469.4	16628.7	4691.9	100.0	100.0	100.0
$\sigma_{C_{1,2}}$	53.2	78.9	29.0	83.9	1464.7	99.2	31.4	0.6	0.9	0.5

^a Ratio of the organic solvent volume (IPA) to the aqueous volume.

^b Not available.

^c Weighed concentration of each ion in de-ionized water (ppm).

^d Determined concentration of each ion in de-ionized water by IC (ppm).

Table 13
Precipitation measurements for groups 1, 2, 3, 4, 5 and 6 (nitrate, phosphate, sulfate, fluoride, nitrite and carbonate) of the NCAW stream using IPA

V_r^a	$\%P/\sigma_p$									
	Al	PO ₄	F	SO ₄	NO ₃	Na	K	Cs	Ca	Sr
0.025	99.8	95.3	87.0	72.3	4.8	n.a. ^b	n.a.	3.9	n.a.	n.a.
	2.0E–2	3.0E–2	4.9E–1	1.7E–1	1.1E0			7.3E–1		
0.050	>99.9	94.3	98.9	31.8	10.2	1.1	1.2	13.5	54.5	69.1
		3.6E–2	6.8E–3	4.3E–1	1.0E0	8.3E–1	9.3E–1	6.5E–1	1.8E0	2.1E–1
0.100	98.6	93.7	82.0	17.1	17.1	7.9	6.2	23.2	93.1	>99.9
	2.3E–2	2.1E–2	3.9E–1	5.2E–1	9.6E–1	7.8E–1	8.9E–1	5.8E–1	8.8E–2	
0.200	98.0	93.8	75.5	25.2	24.1	14.5	9.9	56.2	96.2	>99.9
	3.9E–2	3.9E–2	9.9E–1	4.7E–1	8.7E–1	7.2E–1	8.5E–1	3.3E–1	4.9E–2	
0.400	98.4	92.6	79.5	36.5	30.0	20.7	20.8	76.7	98.5	>99.9
	2.2E–2	6.7E–1	2.0E–1	4.0E–1	7.8E–1	6.7E–1	7.5E–1	1.8E–1	1.9E–2	
0.600	99.1	93.6	84.5	48.8	32.6	31.9	21.2	85.1	>99.9	>99.9
	1.6E–1	1.3E–1	7.6E–1	3.2E–1	7.6E–1	5.7E–1	7.5E–1	1.1E–1		
0.800	99.2	95.2	94.4	74.8	36.2	34.2	23.7	89.1	>99.9	>99.9
	4.6E–2	6.3E–1	1.3E–1	1.6E–1	8.0E–1	5.5E–1	7.2E–1	3.5E–1		
1.000	99.8	91.2	98.0	87.4	50.1	54.0	38.6	n.a.	>99.9	>99.9
	4.1E–2	5.5E–1	9.6E–2	7.9E–2	5.6E–1	3.9E–1	5.8E–1			
$C_{1,2}^c$	11602.7	2374.3	1691.0	14409.0	104033.1	37072.2	4693.9	100.6	99.9	101.9
$C_{1,2}^d$	11600.8	2373.9	1690.9	14409.9	111933.9	37098.1	4693.9	108.7	114.4	100.0
$\sigma_{C_{1,2}}$	115.6	10.6	7.4	63.6	1584.5	221.2	43.2	0.6	1.0	0.6

^a Ratio of the organic solvent volume (IPA) to the aqueous volume.

^b Not available.

^c Weighed concentration of each ion in de-ionized water (ppm).

^d Determined concentration of each ion in de-ionized water by IC (ppm).

Table 14
Precipitation measurements for the species of the NCAW stream using IPA

V_r^a	%P/ σ_p								
	Al	PO ₄	F	SO ₄	NO ₂	NO ₃	Na	K	Cs
0.1	7.1	94.6	96.3	26.0	11.7	0.6	2.5	0.7	2.4
	2.6E0	3.3E-1	8.3E-1	5.0E-1	2.0E0	1.1E0	1.0E0	1.0E0	8.3E-1
0.2	6.5	90.3	97.8	35.3	10.4	1.6	4.1	1.8	7.5
	3.3E0	5.9E-1	2.4E-1	4.3E-1	2.0E0	1.1E0	1.0E0	1.0E0	7.0E-1
0.4	6.8	88.8	98.8	38.9	16.3	1.9	4.8	n.a. ^b	8.1
	2.1E0	6.8E-1	3.5E-1	4.1E-1	1.9E0	1.1E0	9.9E-1		6.9E-1
0.6	6.6	89.8	98.8	46.1	n.a.	1.4	5.6	3.1	9.5
	3.1E0	6.2E-1	2.5E-2	3.6E-1		1.1E0	9.7E-1	1.0E0	6.8E-1
0.8	3.9	90.4	99.8	47.8	n.a.	n.a.	6.6	5.0	n.a.
	2.0E0	5.8E-1	4.8E-3	3.5E-1			1.1E0	1.0E0	
1.0	11.9	91.3	>99.9	52.3	20.3	3.1	13.8	10.5	18.1
	2.0E0	5.3E-1		3.2E-1	1.8E0	1.1E0	8.9E-1	9.4E-1	6.2E-1
1.4	13.5	95.3	>99.9	65.4	21.4	7.8	16.2	11.7	19.5
	3.6E0	2.9E-1		2.3E-1	1.8E0	1.0E0	8.6E-1	9.3E-1	6.1E-1
2.0	19.2	94.3	99.1	92.0	18.1	8.2	18.7	n.a.	20.4
	2.0E0	3.5E-1	1.8E-2	5.4E-2	1.8E0	1.0E0	8.4E-1		6.0E-1
$C_{1,2}^c$	11602.1	2374.3	1690.9	14408.3	19783.6	103487.3	115238.6	4692.0	66.6
$C_{1,2}^d$	11600.8	2402.5	1788.6	14350.6	17716.8	104311.2	115482.7	4908.1	73.3
$\sigma_{C_{1,2}}$	159.0	145.7	45.6	72.3	417.9	823.7	966.9	39.8	1.0

^a Ratio of the organic solvent volume (IPA) to the aqueous volume.

^b Not available.

^c Weighed concentration of each ion in de-ionized water (ppm).

^d Determined concentration of each ion in de-ionized water by IC (ppm).

Table 15
Precipitation measurements for the species of the NCAW stream using EA

V_r^a	%P/ σ_P								
	Al	PO ₄	F	SO ₄	NO ₂	NO ₃	Na	K	Cs
0.1	14.5	>99.9	95.4	31.2	19.2	5.5	13.6	8.6	n.a. ^b
	2.6E0		2.6E-1	8.3E-1	1.8E0	1.1E0	8.9E-1	2.3E0	
0.2	17.2	>99.9	98.9	39.0	20.3	6.9	17.3	15.4	2.2
	1.9E0		3.2E-2	6.7E-1	1.8E0	1.0E0	8.5E-1	1.6E0	7.4E-1
0.6	n.a.	>99.9	98.3	54.3	n.a.	8.6	n.a.	n.a.	14.8
				6.2E-2	3.2E-1		1.1E0		5.1E-1
0.8	35.9	>99.9	98.5	70.0	44.8	37.4	40.2	33.9	45.0
		1.3E0	3.0E-2	3.3E-1	1.2E0	7.4E-1	6.1E-1	6.9E-	4.8E-1
1.0	43.1	>99.9	98.0	81.4	56.8	49.7	51.1	44.2	52.2
	9.8E-1		2.4E-1	3.2E-1	2.4E0	4.8E-1	5.0E-1	5.9E-1	3.7E-1
1.4	52.9	>99.9	99.2	89.0	64.5	59.2	56.6	53.1	56.0
	8.7E-1		4.0E-1	3.2E-1	8.1E-1	6.6E-1	4.5E-1	4.9E-1	7.6E-1
2.0	70.2	>99.9	99.2	95.6	68.1	65.2	66.6	59.1	71.1
	5.5E-1		1.1E-1	4.6E-1	1.2E0	5.0E-1	3.4E-1	4.3E-1	6.8E-1
$C_{1,2}^c$	11602.1	2374.3	1690.9	14408.3	19783.6	103487.3	115238.6	4692.0	66.6
$C_{1,2}^d$	11600.8	2402.5	1788.6	14350.6	17716.8	104311.2	115482.7	4908.1	73.3
$\sigma_{C_{1,2}}$	159.0	145.7	45.6	72.3	417.9	823.7	966.9	39.8	1.0

^a Ratio of the organic solvent volume (IPA) to the aqueous volume.

^b Not available.

^c Weighed concentration of each ion in de-ionized water (ppm).

^d Determined concentration of each ion in de-ionized water by IC (ppm).

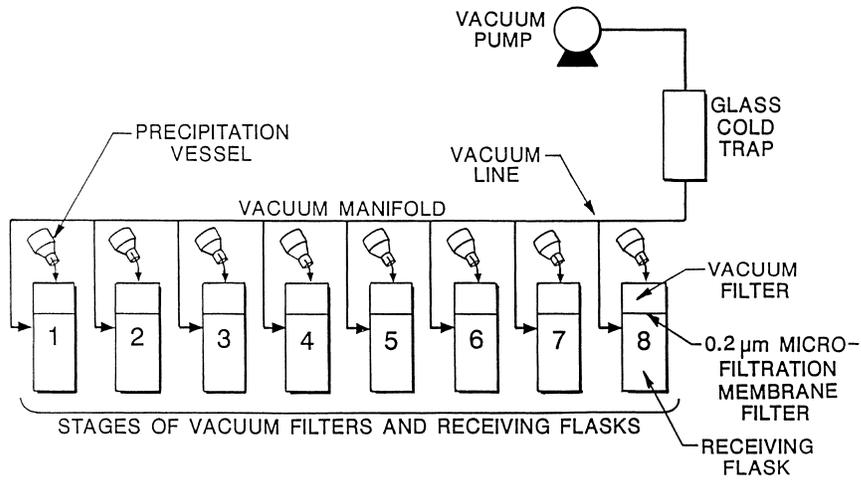


Fig. 1. Schematic diagram of the bench-scale experimental setup.

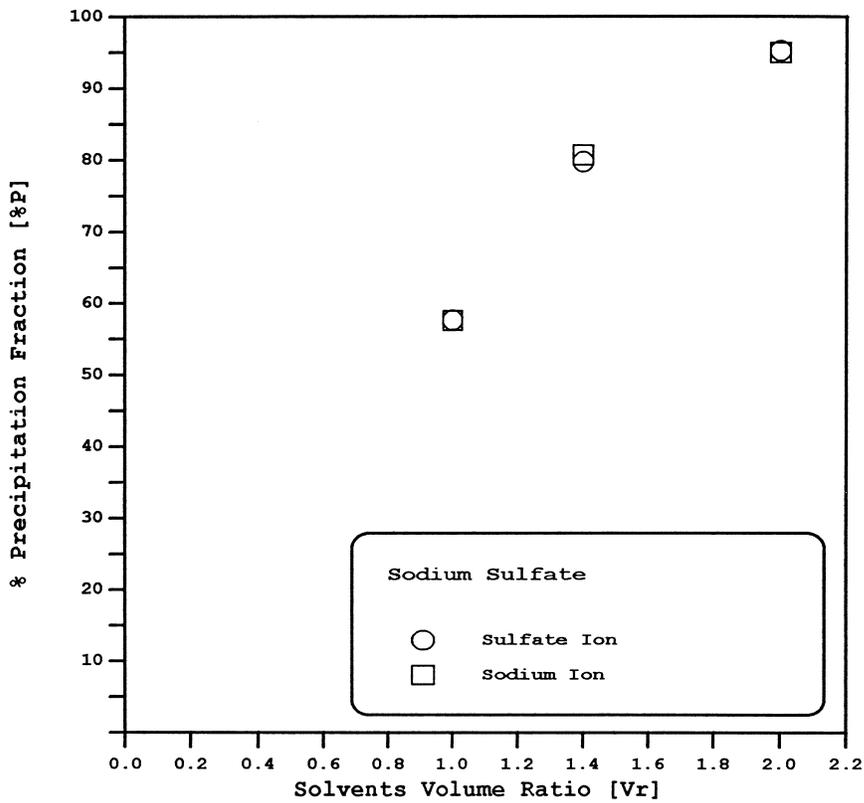


Fig. 2. Precipitation fractions for sodium sulfate system (NCAW stream).

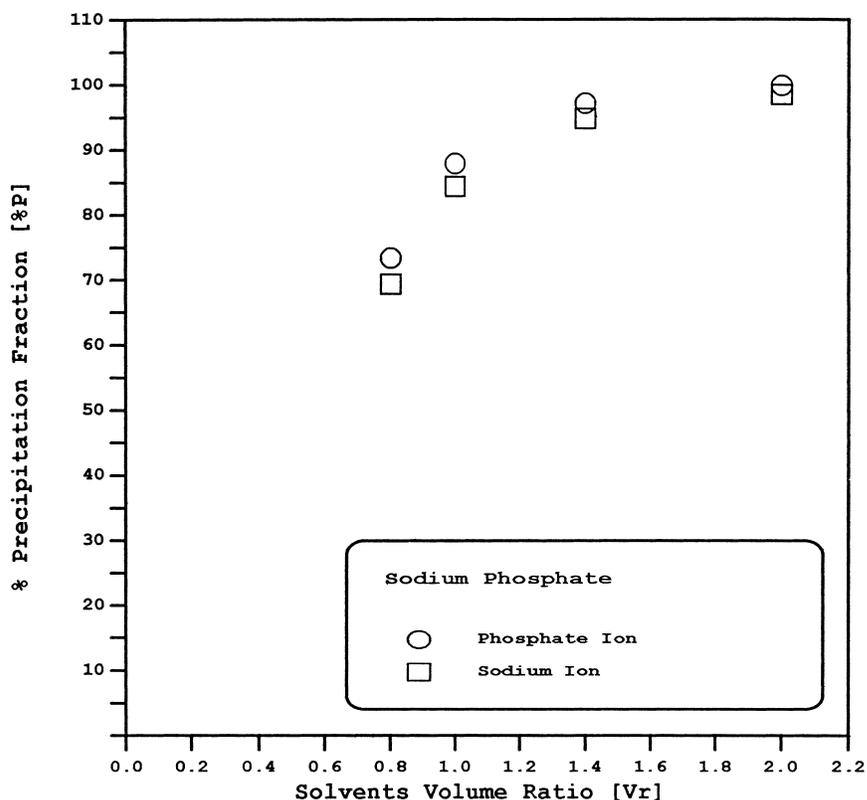


Fig. 3. Precipitation fractions for sodium phosphate system (NCAW stream).

3. Experimental

3.1. Experimental setup and procedure

Recipes of inorganic species reported in Table 1 were used to prepare a stock inactive simulant solution representing the NCAW stream. All chemicals employed in this study were obtained from commercial suppliers, and were used as received and without further purification. A Milli-Q UF-plus (millipore) system combined with a reverse osmosis system was used to provide a highly pure de-ionized water. An accurate electronic balance (A&D company) was used to weigh the inorganic salts (readability: 0.0001 g). The balance was tested prior to each measurement against standard weights with a certification traceable to the National Bureau of Standards.

Eight samples, each of which consists of 20 ml, were drawn from the stock inactive simulant solution and injected into 100 ml precipitation flasks. These eight samples were used to study the precipitation of the targeted species in the presence of different amounts of the organic solvent. Another 20 ml sample was drawn from the stock inactive

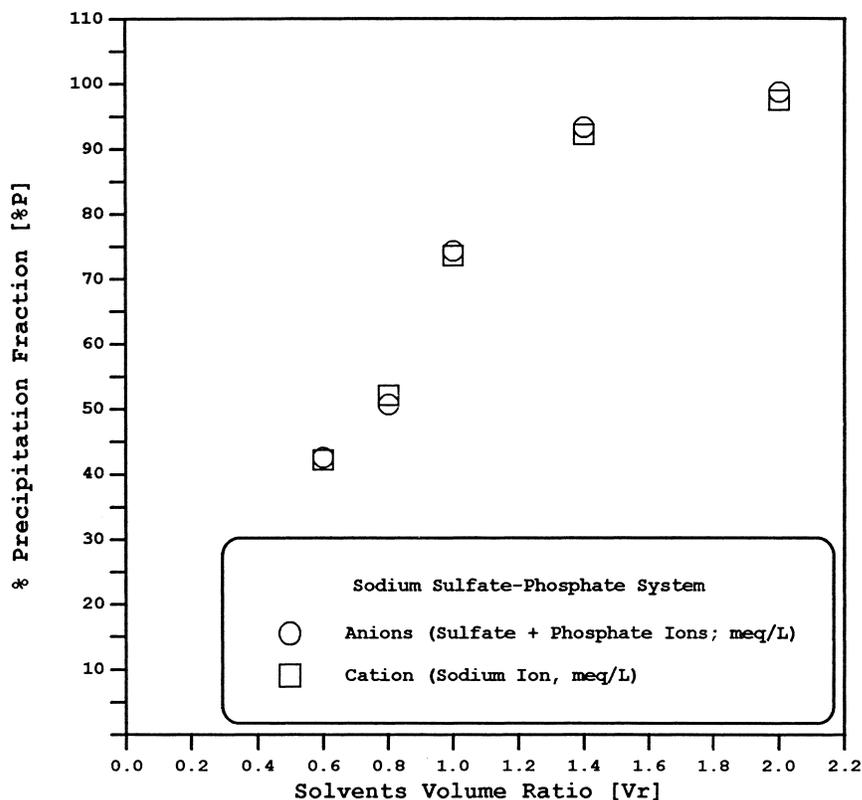


Fig. 4. Precipitation fractions for sodium-sulfate-phosphate system (NCAW stream).

simulant solution and injected into 20 ml microflasks to be used as a reference sample.

Different amounts of IPA or EA (2.0, 4.0, 8.0, 12.0, 16.0, 20.0, 28.0, and 40.0 ml) were then drawn and injected into each of the 20 ml inactive simulants. In some cases, however, a lower range of the amounts of the precipitation solvent were used for precipitation testing (0.5, 1.0, 2.0, 4.0, 8.0, 12.0, 16.0, 20.0 ml). The pH of each sample was measured using an Orion-230A pH meter. These amounts of IPA or EA provided a reasonable range of precipitation measurements without excessive waste of the precipitation solvents.

A schematic diagram of the bench-scale precipitation experimental setup is shown in Fig. 1. For each of the eight samples, formed precipitates were separated from the organic-aqueous solution by vacuum filtration using 0.2 μm dead-end microfiltration membrane filters (Osmonics). The vacuum filtration apparatus is connected to 1000 ml receiving flasks. The receiving flasks were, in turn, connected to a vacuum manifold via vacuum tubes. One end of the manifold is connected to a vacuum pump via a glass cold trap. The glass cold trap is immersed in liquid nitrogen to condense and recover IPA or EA.

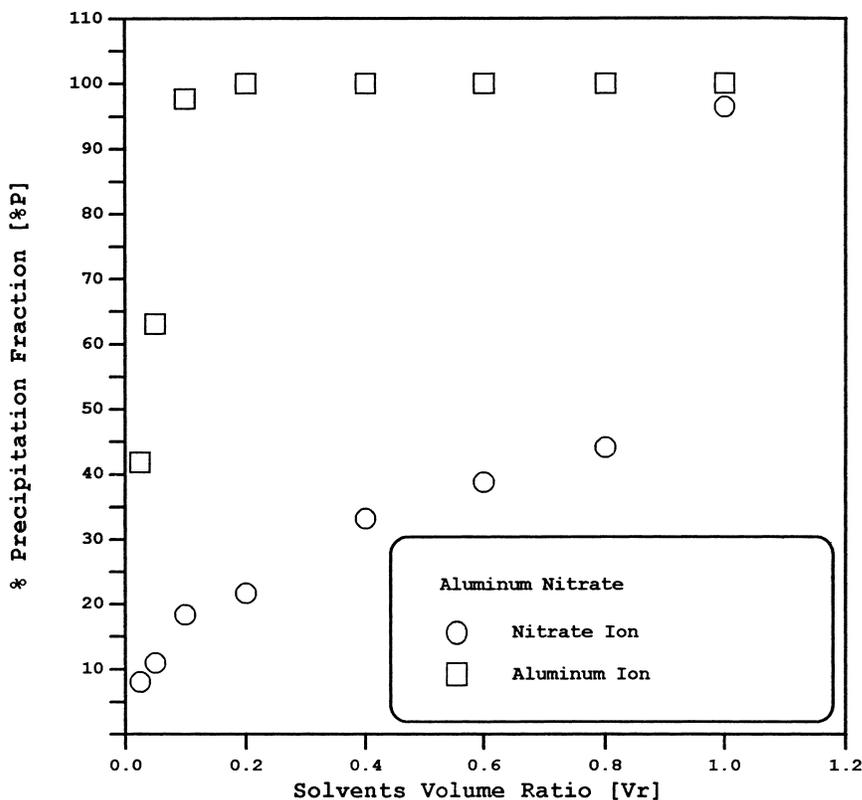


Fig. 5. Precipitation fractions for aluminum nitrate system (NCAW stream).

3.2. Ion chromatography (IC) systems

Three Dionex IC systems series-8100 were used for the analysis of anions, cations–amines, and transition metals (aluminum). All of the three Dionex systems were operated, automated and controlled by the Dionex AI-450 (version 3.33) Chromatography software and three advanced computer interfaces (ACI-3).

The first IC system was used for anions analysis. The IC system is equipped with a conductivity detector (CDM-III), advanced gradient pump (AGP-1), and automated sampler (AS40). IonPac anion separation column (AS12A), IonPac anion guard column (AG12A), and anion self-regenerating suppressor (ASRS-Ultra) were used to analyze anions. EPA method 300.1 was employed as a guideline to determine the concentrations of anions [28].

The second IC system was used for the analysis of the cations and amines (IPA and EA). The system is equipped with a conductivity detector (CDM-III), advanced gradient pump (AGP-1), and automated sampler (AS40). IonPac cation separation column (CS12A), IonPac cation guard column (CG12A), and cation self-regenerating suppressor (CSRS-Ultra) were used for cations and amines analysis. EPA method 300.7 [29] (as a guide) along with

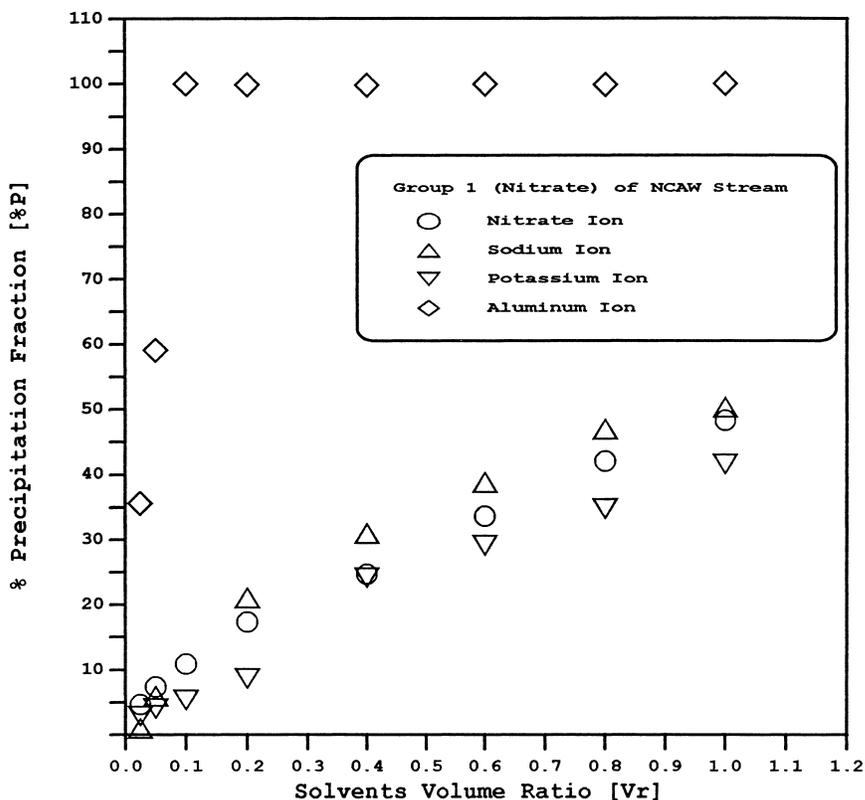


Fig. 6. Precipitation fractions for the non-radioactive species of group 1 (NCAW stream).

the Dionex column application note [30] were used to determine the concentrations of the cations and amines.

The third IC system was used for the analysis of transition metals (aluminum). The system is equipped with a variable wavelength (UV–VIS) detector (VDM-II), advanced gradient pump (AGP-1), and automated sampler (AS30). IonPac cation exchange column (CS5A) for the determination of transition metals with visible absorbance detection along with IonPac cation guard column (CG5A) were used to analyze aluminum. Dionex application note 42 [31] was employed to perform the cation exchange separation, post-column reaction, and visible detection of the aluminum color complex.

Calibration curves for anions, cations, amines, and aluminum were developed. Stock calibration solutions containing 1000 ppm of each species were prepared. For each species, several standard solutions (6–10, depending on the linear range of the species) were then prepared using the stock calibration solution. For each standard, three samples were injected into the IC, and thus the precision could be determined through replication. This procedure was repeated until the calibration data were obtained for the entire linear range of each targeted species. The calibration data were then fitted to straight lines.

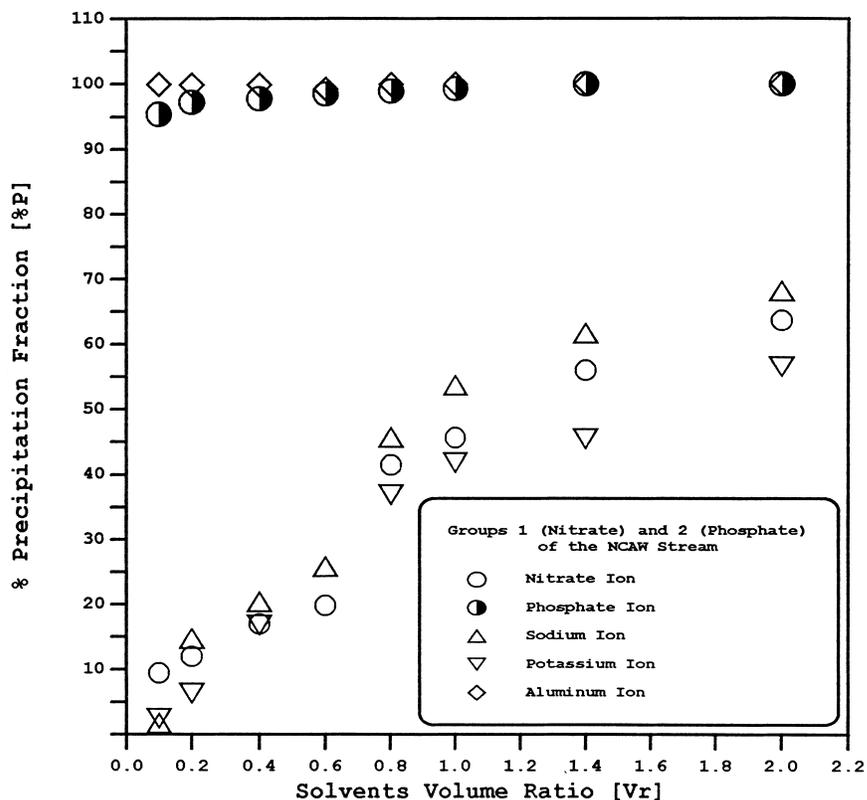


Fig. 7. Precipitation fractions for the non-radioactive species of groups 1 and 2 (NCAW stream).

3.3. Determination of the precipitation fractions and error analysis

The concentrations of most targeted species are much higher than the concentrations within the linear range of their calibration curves. As such, a serial dilution procedure was adapted for the analysis of such targeted species (standard and filtered samples). However, the concentrations of the targeted species in the standard and the filtered samples determine the number of dilution steps. One or two dilution steps were sufficient to carry out the analysis for such species. The serial dilution procedure served two purposes. First, targeted species were analyzed within their linear range of the calibration data. Second, the significant presence of the aluminum ion, for instance, in the standard and filtered samples (particularly in the standard sample) and its effect on the anion separation column and guard was minimized. Thus, the serial dilution procedure was a key element in analyzing the concentrations of the targeted species in the standard and filtered samples.

Once the concentrations of the targeted species in both the reference (aqueous) sample, $C_{1,2}$ or $x_{1,2}$, and the filtered (organic-aqueous) samples, $C_{1,m}$ or $x_{1,m}$, are determined, and

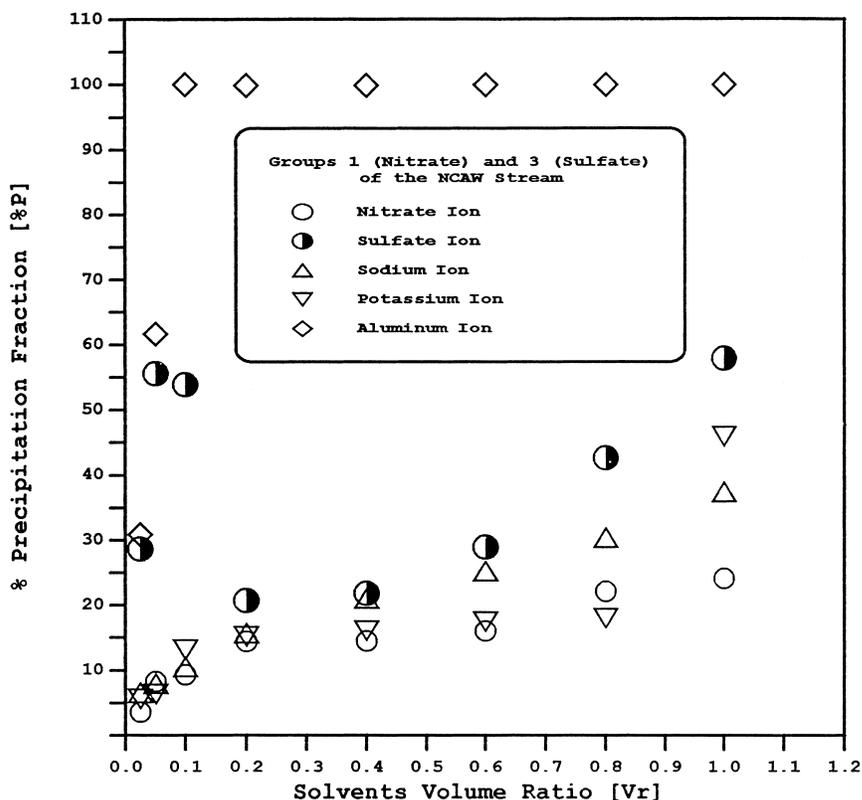


Fig. 8. Precipitation fractions for the non-radioactive species of groups 1 and 3 (NCAW stream).

P can be calculated as follows [23]

$$P = 1 - \frac{C_{1,m}}{C_{1,2}} = 1 - \frac{x_{1,m}}{x_{1,2}} \quad (3)$$

Standard deviations (σ_P) in the experimental values of P due to random variations in the experimental variables was estimated by error propagation methods. Error propagation allows an estimate for the uncertainty interval which should be associated with the experimental results based on the observations in the raw data. Detailed derivation of the σ_P is given elsewhere [23,32].

4. Presentation and analysis of experimental data

To evaluate the viability of the experimental methods and the acquired experimental data, error analysis and instrumental consistency test are essential elements in the overall experimental effort. Although there is no unquestionably correct data, these tests are usually

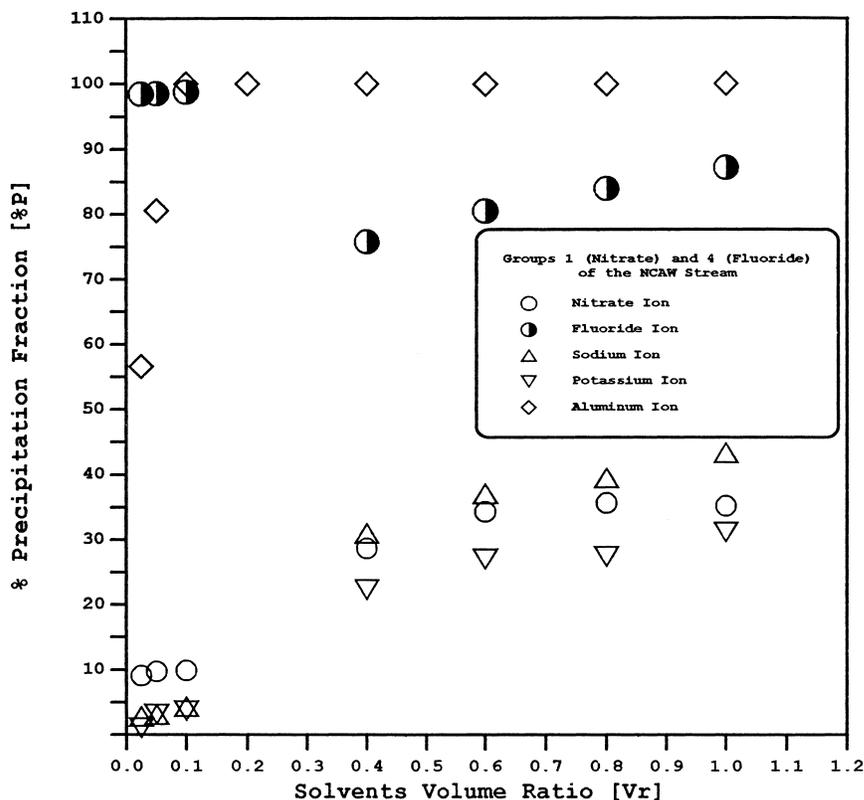


Fig. 9. Precipitation fractions for the non-radioactive species of groups 1 and 4 (NCAW stream).

indicative of the overall quality and provide a means of detecting inconsistency of the reported data. Presentation of the experimental data along with error analysis, assessments for the consistency of the instruments and reported data, discussion of the experimental data, recovery of the precipitation solvents, and evaluation of the solubility framework's equations are discussed below.

4.1. Presentation of the experimental data

The precipitation process can be evaluated in terms of the precipitation fractions (P) as a function of the solvents volume ratio (V_r), that is, the ratio of the organic solvent volume to the aqueous volume. The precipitation data for the tested systems along with their error analysis are presented in Tables 2–15. The data include the solvents volume ratio (V_r), the percent precipitation fractions (% P) and their standard deviations (σ_P), and the concentrations of each targeted species in water ($C_{1,2}$) and their standard deviation ($\sigma_{C_{1,2}}$).

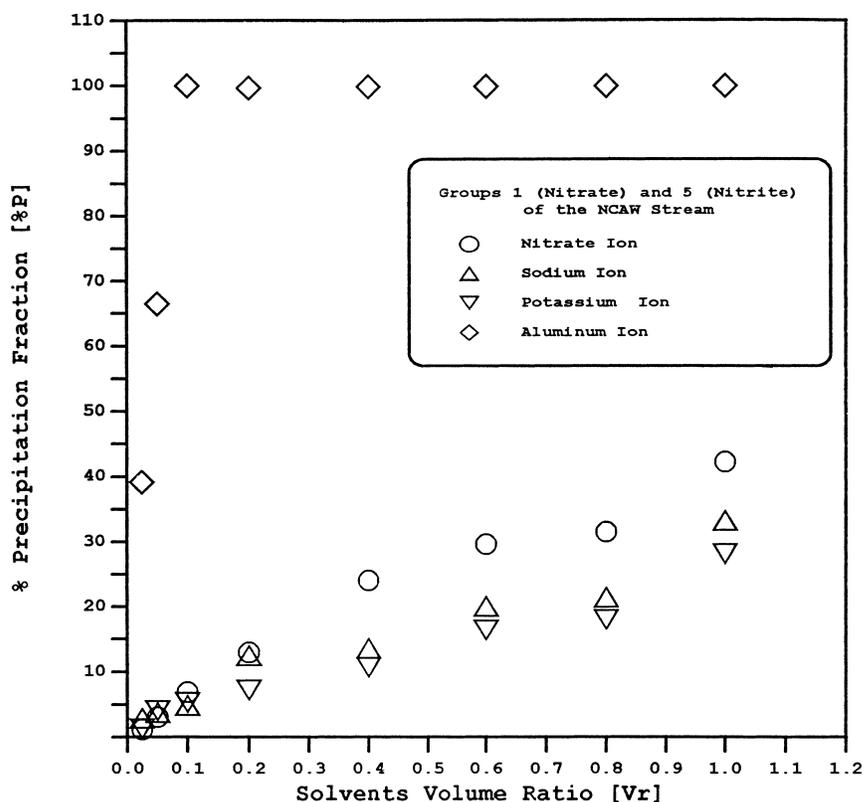


Fig. 10. Precipitation fractions for the non-radioactive species of groups 1 and 5 (NCAW stream).

4.2. Instrumental and experimental procedure consistency

Instrumental consistency for the IC systems were established by frequent calibration. In addition, each of the IC systems was tested by determining the known concentration of the targeted species ($C_{1,2}$) in de-ionized water prior to, and after each set of measurements to ensure proper analysis. The measured (weighed) and the determined (analyzed by the IC systems) concentrations of the targeted species in de-ionized water ($C_{1,2}$) are also given in Tables 2–15. Comparisons of these data indicate good agreement. The observed differences, in most cases, were within the uncertainty of the employed IC systems.

As discussed in the experimental section, three different IC systems were used to analyze anions, cations, and transition metals. As such, to further validate and evaluate the consistency of the IC systems, the precipitation of sodium sulfate, sodium phosphate, sodium-sulfate-phosphate, and aluminum nitrate systems (concentrations as given in Table 1) were also studied using IPA as a precipitation agent. A further objective for this study was to assess the capability of IPA in precipitating these critical compounds individually. It should be pointed out that sodium nitrate, sodium fluoride, sodium hydroxide,

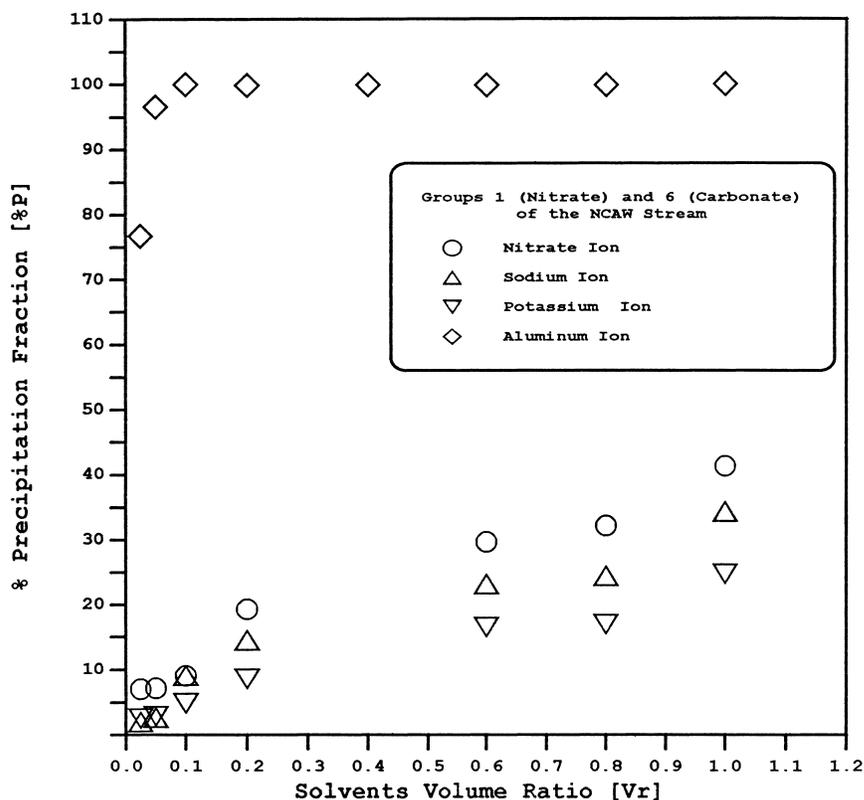


Fig. 11. Precipitation fractions for the non-radioactive species of groups 1 and 6 (NCAW stream).

sodium carbonate, sodium nitrite, and potassium nitrate systems (concentrations as reported in Table 1) were also studied individually using IPA as a precipitation solvent. However, no precipitation for such systems was observed in the tested range of IPA (V_r : 0.1, 0.2, 0.4, 0.6, 0.8, 1.0, 1.4, and 2.0).

As shown in Table 2 and Fig. 2 reveal that the P values of phosphate ion (2374 ppm) and sodium ion (1724 ppm) from sodium phosphate system were also identical and extended between a V_r of 0.8 (% P : 70.7) and V_r of 2.0 (% P : 99.9). No precipitation was observed for phosphate and sodium ions below a V_r of 0.8. These precipitation studies indicate that the two IC systems that were used to analyze anions and cations separately were very consistent.

The P values of phosphate ion (2374 ppm), sulfate ion (14,410 ppm), and sodium ion (8622 ppm) from sodium-sulfate-phosphate system is presented in Table 4. The P values of phosphate ion (% P : 89.9 at $V_r = 0.6$ –99.9 at $V_r = 2.0$) and sulfate ion (% P : 30.7 at $V_r = 0.6$ –98.4 at $V_r = 2.0$) from sodium-sulfate-phosphate system were higher than the P values of phosphate ion from sodium phosphate system (Table 3) or the P values of sulfate ion from sodium sulfate system (Table 2). The material balance (in terms of meq./l) between the total anions (phosphate and sulfate) and the cation (sodium) reveals that the removal of

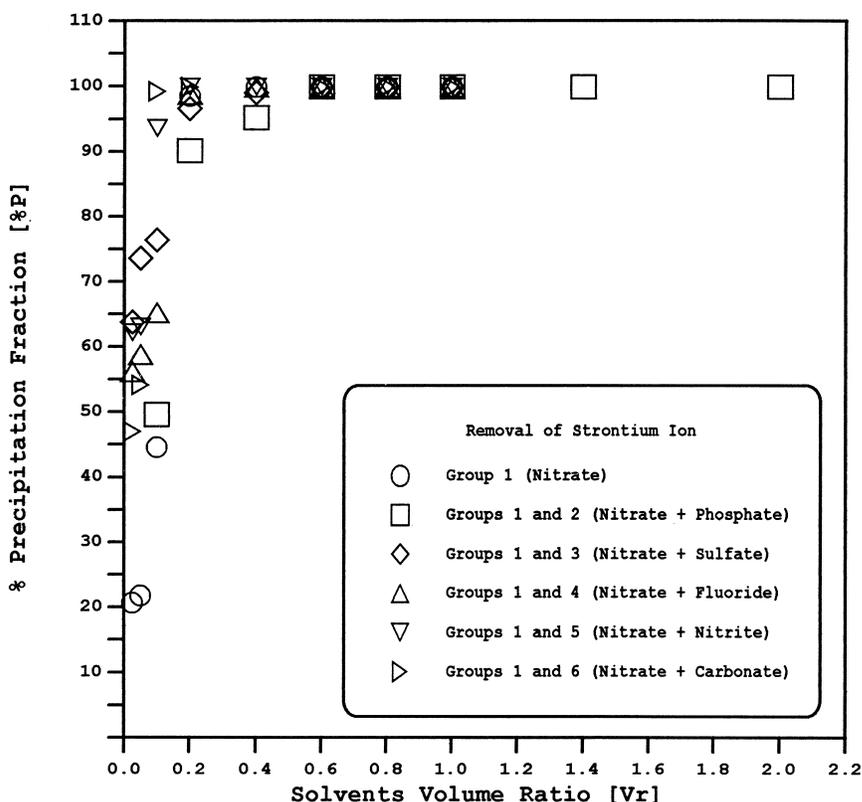


Fig. 12. Precipitation fractions for the strontium ion (NCAW stream).

the total anions were equivalent to the removal of the cation. This would demonstrate the excellent instrumental consistency of the two IC systems that were employed separately for the analysis of anions and cations. Fig. 4 depicts the P values (in terms of meq./l) of the combined anions (phosphate and sulfate) and the sodium ion.

The P values of aluminum ion (11,602 ppm) and nitrate ion (79,986 ppm) from aluminum nitrate system (concentrations as reported in Table 1) over a V_r range extended from 0.025 to 1.0 using IPA were also studied. The P values are presented in Table 5 and depicted in Fig. 5. The P values of the aluminum ion were reached an asymptotic value (% P : 99.9) at a V_r of 0.2, while the P values of the nitrate ion were significantly lower than the P values of the aluminum ion. However, the P values of the nitrate ion increased with the increase in the amount of IPA. This situation is likely to be attributed to the fact that aluminum nitrate decomposes in water to produce a basic nitrate with some of the nitrate present as: $\text{Al}(\text{OH})(\text{NO}_3)_2$. Upon the addition of IPA, the aqueous solubility of the aluminum ion was drastically suppressed and thus the aluminum ion was substantially precipitated. Hydrous oxide would fill the gap of the precipitated aluminum ion by forming a basic nitrate [33], which would lead to the observed low precipitation of the nitrate ion compared to the aluminum ion.

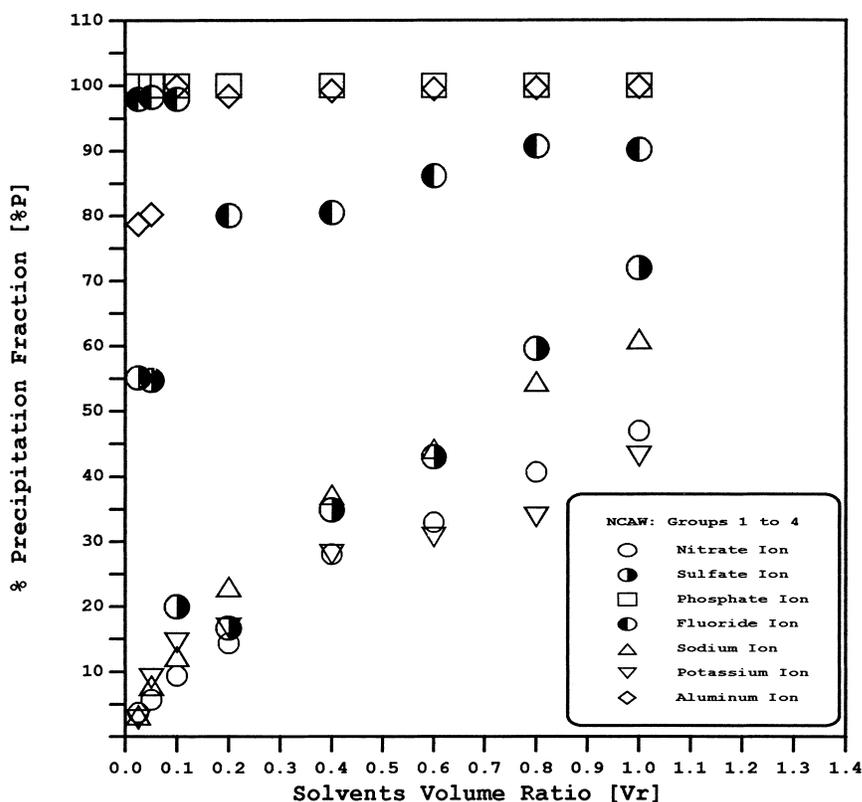


Fig. 13. Precipitation fractions for the non-radioactive species of groups 1, 2, 3 and 4 (NCAW stream).

Certain transition metals such as aluminum, iron, and zirconium form complexes with fluoride and phosphate, in particular. Such a complex formation changes the positive charges of the ions (lower positive charge) or converts them to negatively charged species [33,34], which would hinder the IC detection capabilities for such anions. For instance, the presence of aluminum, in particular, or iron often results in tailing of the sulfate peak and complete disappearance of the phosphate peak [34]. The reason for emphasizing this problem is that in our review of several DOE waste processing reports, attention was not given to this problem, which may indicate that the analysis of phosphate, in particular, were possibly erroneous in some reports. In this work, however, this problem was resolved by using On-Guard-H cartridges (Dionex) that contains styrene-based, strong acid resin, which is designed to remove high levels of multivalent cations and transition metals from samples before injection into the IC [35]. The possible contamination of the column and guard was monitored by running standards before and after the analysis of the anions samples. The On-Guard-H resin was found to be effective in protecting the anion separation column from contamination with aluminum ion, and thus allowed acceptable analysis for the fluoride, phosphate, and sulfate ions.

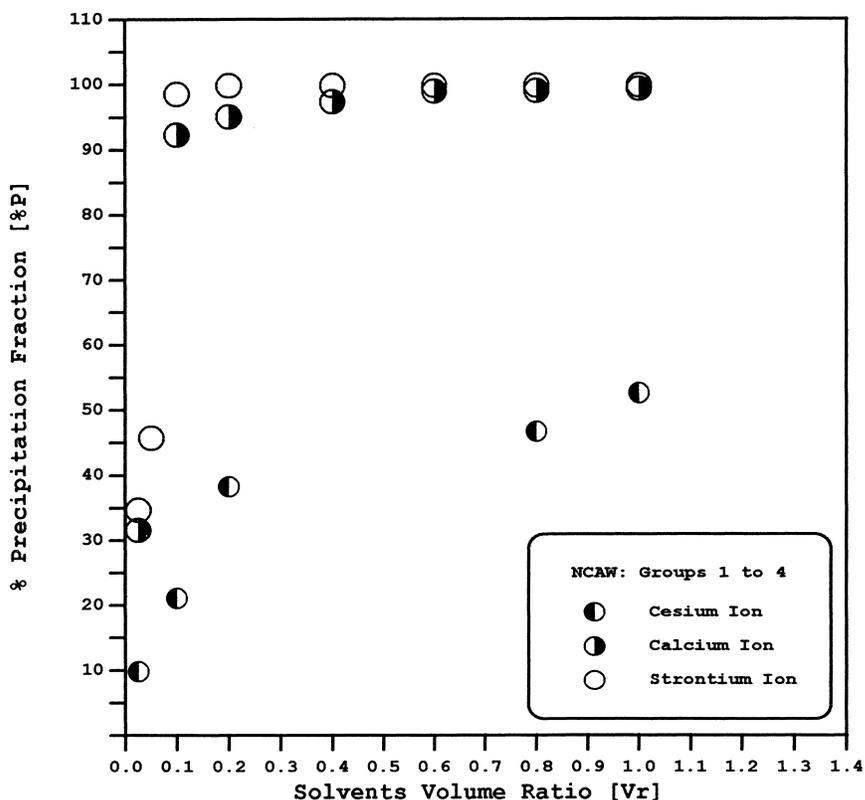


Fig. 14. Precipitation fractions for the cesium, calcium and strontium ions of groups 1, 2, 3 and 4 (NCAW stream).

The above discussed instrumental consistency tests were taken as a confirmation of acceptable consistency among the three IC systems (for the analysis of anions, cations, and transition metals) as well as the employed experimental procedures (e.g. calibration curves, dilution steps, and column and guard contamination), and thus reasonable analysis of the precipitation measurements.

4.3. Discussion of the experimental data

The precipitation of radioactive and non-radioactive species from the DOE neutralized current acid waste (NCAW) stream was studied. Table 1 presents the species profile of the NCAW stream. As shown in Table 1, cations and anions species were reported in terms of their possible basic compounds. The compounds were then divided into seven groups (nitrate, phosphate, sulfate, fluoride, nitrite, carbonate, and hydroxide). The nitrate group, which is the major anion in the DOE waste streams, contains in most cases all cations, while the rest of the groups are only in the form of sodium. The NCAW stream contains appreciable concentrations of the critical anions (sulfate, phosphate and fluoride), radioactive species

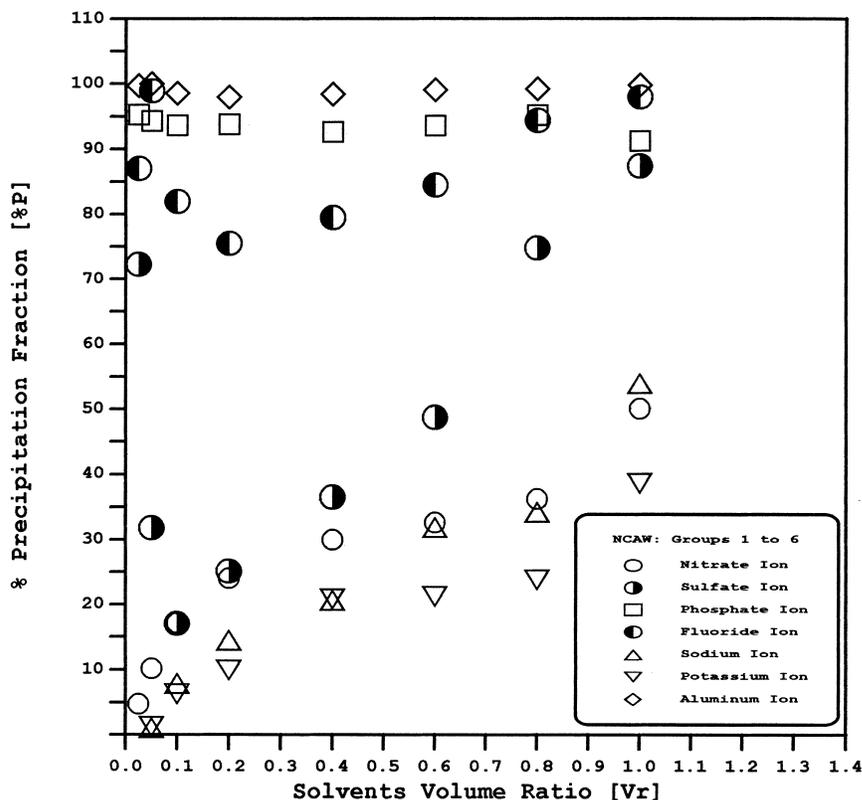


Fig. 15. Precipitation fractions for the non-radioactive species of groups 1, 2, 3, 4, 5 and 6 (NCAW stream).

(cesium) as well as other non-radioactive species (aluminum, sodium, potassium, nitrate, nitrite, carbonate, and hydroxide), which makes it ideal for extensive testing of the feasibility of the precipitation concept. As such, precipitation measurements were conducted on the: (1) nitrate group alone (Table 6); (2) binary groups containing the groups of nitrate–phosphate (Table 7), nitrate–sulfate (Table 8), nitrate–fluoride (Table 9), nitrate–nitrite (Table 10), and nitrate–carbonate (Table 11); (3) combined nitrate, phosphate, sulfate, and fluoride groups (Table 12); (4) combined nitrate, phosphate, sulfate, fluoride, nitrite, and carbonate groups (Table 13) and (5) simulated NCAW stream (Tables 14 and 15).

It should be pointed out that an intensive brown gas was formed when the nitrate group (contains appreciable concentration aluminum nitrate) was mixed with the nitrite group (sodium nitrite). In such an aqueous mixture [33], aluminum nitrate hydrolyzes in water to produce a basic nitrate and nitric acid



The addition of sodium nitrite produces nitrous acid



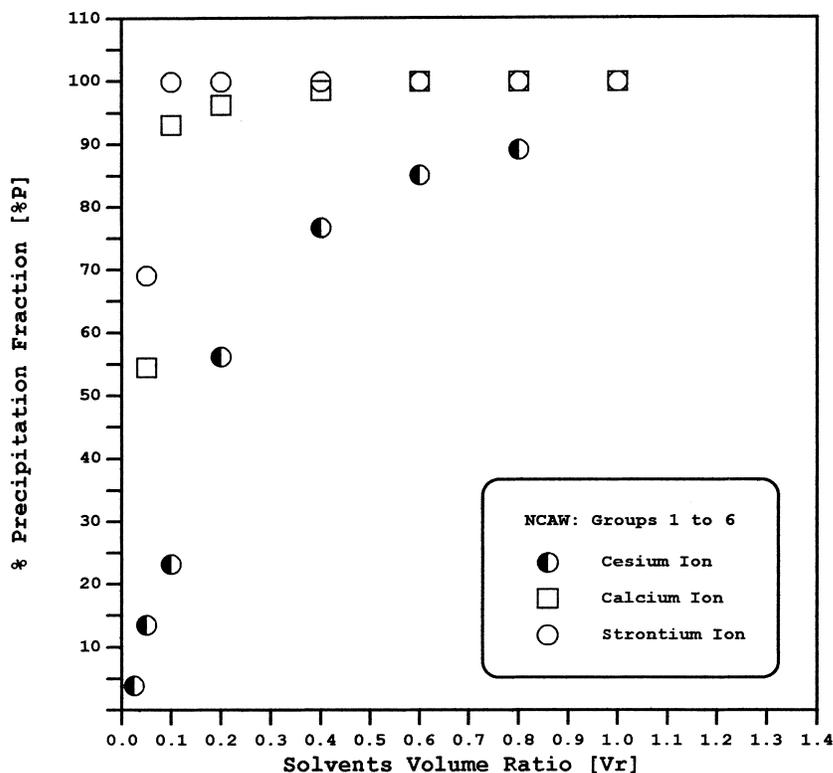


Fig. 16. Precipitation fractions for the cesium, calcium and strontium ions of groups 1, 2, 3, 4, 5 and 6 (NCAW stream).

Nitrous acid is very unstable and yields nitrous oxide (NO)



The “NO” on contact with air instantly oxidizes to NO_2 (brown gas)



As shown in Tables 10 and 13, a significant increase in the concentrations of the nitrate ion, and almost a complete depletion of the nitrite ion (converted to nitrate and NO_2 brown gas) were occurred. This may suggest that with some acid wastes, a significant generation of NO_2 (gas) is expected.

In the case of alkaline wastes, aluminum nitrate dissolves as follows:



Since the waste is basic, the only source of “NO” is from the decomposition of sodium nitrite



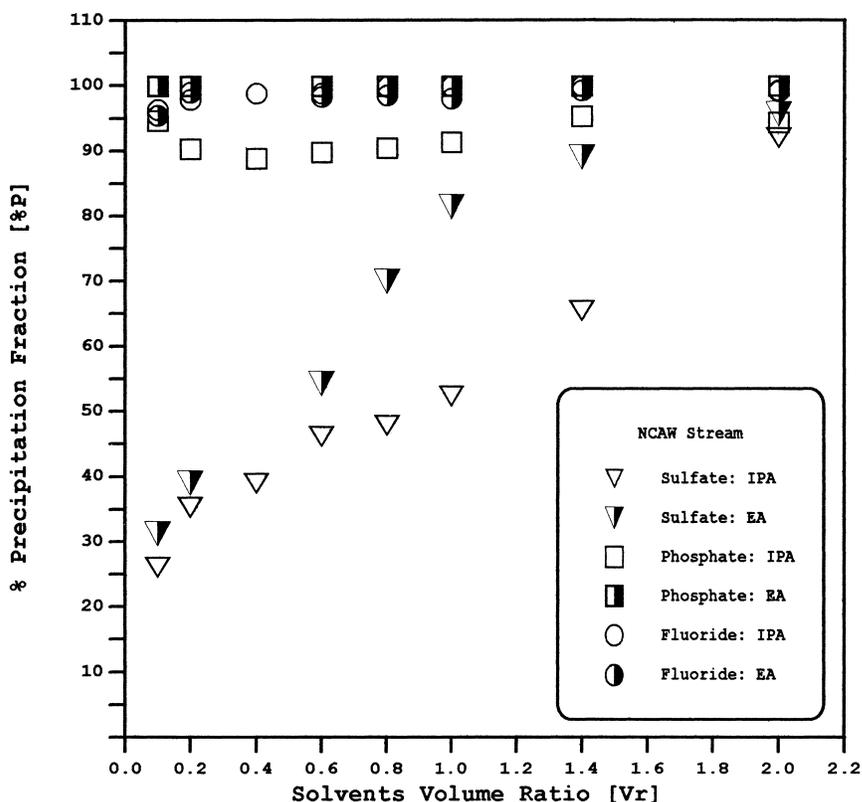


Fig. 17. Precipitation fractions for the critical anions from the NCAW stream.

If such a reaction is reversible, a little amount of “NO” will be released (due to the high concentrations of sodium hydroxide and sodium nitrate). Indeed, this was the case in formulating the NCAW stream. As shown in Tables 14 and 15 (see Table 1), a small decrease in the initial concentrations of the nitrite ion was observed due to the slight formation of a brown gas (NO_2).

In the cases of studying the precipitation of species from the nitrate group alone (Table 6), and from the binary groups (nitrate–phosphate, nitrate–sulfate, nitrate–fluoride, nitrate–nitrite, nitrate–carbonate: Tables 7–11), the following precipitation trends were observed. It should be mentioned, however, that these groups were purposely spiked with a 100 ppm of cesium ion (cesium nitrate, all groups), a 100 ppm of strontium ion (strontium nitrate, all groups), and a 100 ppm of calcium ion (calcium nitrate, some groups). The P values of aluminum ion were extremely high. In most cases (except in the case of nitrate–fluoride group), the P values of aluminum ion were reached an asymptotic value (>99.9) at a V_r of 0.1. The precipitation values of the nitrate ion in all cases were moderately low ($\%P$: ≈ 46 at V_r : 1.0). The lowest P values of the nitrate ion were observed in the case of the nitrate–sulfate group ($\%P$: 3.6–24.1 at between V_r : 0.1 and 1.0). However, the highest P

Table 16
Recovery of IPA from the NCAW and de-ionized water

V_3^a (ml)	C_3^b (ppm)	NCAW		De-ionized water	
		C_3^c	% R^d	C_3^c	% R^d
2.0	69544.1	847.0	98.8		
4.0	139088.2	1364.8	99.0	74172.3	46.7
8.0	278176.3	1624.4	99.4	73686.1	73.5
12.0	417264.5	2392.9	99.4		
16.0	556352.6	3645.3	99.3	79016.6	85.8
20.0	695440.7	11640.0	98.3	778655.7	94.4
28.0	973617.0	20071.2	97.9		
40.0	1390882.0	21866.1	98.4		

^a Volume of IPA (ml).

^b Concentration of IPA (ppm).

^c Remaining concentration of IPA in the sample after applying vacuum (ppm).

^d Percent of removed IPA.

values of the nitrate ion were observed in the cases of the nitrate group alone (% P : 4.7–48.3 at V_T : 0.025–1.0), and the nitrate–phosphate group (% P : 9.5–63.7 at between V_T : 0.1 and 2.0). The P values of the non-radioactive alkali cations (sodium and potassium) were also moderately low in all cases, and their P values were relatively in parallel to the P values of the nitrate ion. The highest P values for the alkali cations were observed in the case of the nitrate–phosphate group. In some cases, the P values of cesium ion were higher than the P values of sodium and potassium ions, and the highest P values for cesium ion were observed in the cases of the nitrate–sulfate and nitrate–fluoride groups. The P values of alkaline cations (strontium and calcium) were generally very high (% P : reached 99.9). The P values of phosphate ion from the nitrate–phosphate group (Table 7) were very high and

Table 17
Recovery of EA from the NCAW and de-ionized water

V_3^a (ml)	C_3^b (ppm)	NCAW		De-ionized water	
		C_3^c	% R^d	C_3^c	% R^d
2.0	80466.7	789.8	99.0		
4.0	160933.4	1092.7	99.3	101326.5	37.0
8.0	321866.8	n.a. ^e	n.a.	114898.4	64.3
12.0	482800.2	4049.7	99.2		
16.0	643733.6	4506.1	99.3	110961.0	82.8
20.0	804667.0	16898.0	97.9	108312.5	86.5
28.0	1126533.8	66465.5	94.1		
40.0	1609334.0	93341.4	94.2		

^a Volume of IPA (ml).

^b Concentration of IPA (ppm).

^c Remaining concentration of IPA in the sample after applying vacuum (ppm).

^d Percent of removed IPA.

^e Not available.

Table 18

The 2-Suffix equation (Eq. (1)) representation of the cation species from the selected and tested anion groups of the simulated NCAW stream using IPA

System	Model's parameters		RMSE	%AAD	NP
	C_1^a	C_2^b			
Sodium ion					
Group 1	-1.4495	0.4688	0.0157	3.40	6
Groups 1 and 2	-2.7877	10.152	0.0654	15.96	8
Groups 1 and 3	-2.0274	-3.8679	0.0441	13.23	7
Groups 1 and 4	-1.9115	4.8490	0.0497	21.20	7
Groups 1 and 5	-0.3751	-1.2282	0.0501	20.93	8
Groups 1 and 6	-0.2603	-2.9038	0.0439	9.77	6
Groups 1–4	-0.2076	2.1828	0.0281	5.03	8
Groups 1–6	-1.3900	2.1733	0.0985	12.30	6
Potassium ion					
Group 1	-0.9944	0.0517	0.0215	6.26	6
Groups 1 and 2	-1.9102	3.3736	0.0396	6.13	7
Groups 1 and 3	1.0621	-4.7961	0.0265	16.92	7
Groups 1 and 4	-1.2054	1.4413	0.0344	16.60	7
Groups 1 and 5	-0.3751	-0.3008	0.0381	16.36	8
Groups 1 and 6	-0.2485	-0.7337	0.0252	14.10	7
Groups 1–4	-0.5681	-1.4493	0.0393	15.75	8
Groups 1–6	-0.7848	0.2530	0.0587	13.75	6
Cesium ion					
Group 1	-0.1601	-3.0127	0.0787	11.77	5
Groups 1 and 2	-0.8940	-1.8710	0.0752	11.18	4
Groups 1 and 3	0.2422	-5.2452	0.0398	9.66	4
Groups 1 and 4	-3.2745	-1.6525	0.1434	15.43	7
Groups 1 and 5	-8.3876	7.8192	0.2672	37.54	4
Groups 1 and 6	3.2678	-0.9437	0.0721	20.63	5
Groups 1–4	0.7605	-5.0377	0.0514	13.00	5
Groups 1–6	-11.110	11.195	0.2057	18.24	7

^a $C_1 = \ln(x_{1,3}/x_{1,2})$.

^b $C_2 = \Lambda_{32}$.

reached an asymptotic value (% P : >99.9) at a V_r of 1.4. The P values of sulfate ion from the nitrate–sulfate group (Table 8) were moderately low (% P : 28.7 at V_r : 0.025; % P : 57.9 at V_r : 1.0). The P values of fluoride ion from the nitrate–fluoride group (Table 9) were relatively high (% P : 75.9–98.8). Figs. 6–11 show the precipitation fractions of the non-radioactive species in the tested groups. The precipitation fractions of strontium are shown in Fig. 12.

The removal of key non-radioactive anions (nitrate, phosphate, sulfate, and fluoride) as well as aluminum, cesium and strontium is very critical to minimize both the HLW and LLW. The precipitation of these four critical anion groups (e.g. acid-dissolved sludge and acidified supernate) as reported in Table 1 using IPA was studied. It should be pointed out that this group was also purposely spiked with a 100 ppm of each of cesium ion (cesium nitrate), strontium ion (strontium nitrate), and calcium ion (calcium nitrate). As given in Table 12, the non-radioactive species (aluminum, phosphate and fluoride ions) can be effectively removed (>99.9%) by IPA at low values of V_r (0.025–0.1). However, the P values of the sulfate ion

Table 19

The 2-Suffix equation (Eq. (1)) representation of the anion species from the selected and tested anion groups of the simulated NCAW stream using IPA

Stream	Model's parameters		RMSE	%AAD	NP
	C_1^a	C_2^b			
Nitrate ion					
Group 1	-0.7450	-2.0661	0.0537	14.97	8
Groups 1 and 2	-1.3830	2.6016	0.1491	27.76	7
Groups 1 and 3	0.3979	-4.9089	0.0416	21.44	8
Groups 1 and 4	-0.0682	-5.5249	0.0281	18.24	7
Groups 1 and 5	-1.2252	1.6087	0.0311	5.52	6
Groups 1 and 6	-0.3257	-3.7776	0.0428	18.25	7
Groups 1–4	-1.1073	-0.1621	0.0302	10.57	8
Groups 1–6	1.3418	-6.7523	0.0831	11.92	8
Sulfate ion					
Groups 1 and 3	-0.5190	-2.1944	0.3930	48.94	8
Groups 1–4	-2.5345	3.0921	0.3990	40.47	8
Groups 1–6	-2.7286	2.2308	0.5822	39.78	8

^a $C_1 = \ln(x_{1,3}/x_{1,2})$.

^b $C_2 = A_{32}$.

were lower than the P values of the phosphate and fluoride ions but higher than the P values of nitrate ion. The P values of alkaline cations (calcium and strontium) were very high at a V_r of 0.1, and the P values of strontium were reached an asymptotic values (>99.9%) in the V_r range of 0.2–1.0. The P values of alkali cations (sodium, potassium, and cesium) were relatively about the P values of nitrate ion, and thus they were significantly lower than the P values of alkaline cations. Fig. 13 shows the P fractions of the non-radioactive species. The precipitation fractions of the cesium, strontium, and calcium ions are shown in Fig. 14.

As presented in Table 13, the precipitation of combined nitrate, phosphate, sulfate, fluoride, nitrite, and carbonate groups was also studied using IPA. The purpose of this study was to evaluate the precipitation of these six groups from the NCAW stream in the absence of the hydroxide group. These six groups were also spiked with a 100 ppm of each of cesium ion (cesium nitrate), strontium ion (strontium nitrate), and calcium ion (calcium nitrate). The P values of the aluminum ion (% P : 98.0 to >99.9) were very high in the whole range of the V_r values. The P values of the phosphate ion (% P : 91.2–95.3) and fluoride ion (% P : 75.5–98.9) were significantly high, while the P values of the sulfate ion (% P : 17.1–87.4) were moderately high. The P values of the nitrate ion (% P : 4.8 and 50.1) were moderately low. In general, the P values of alkaline cations were significantly higher than the P values of alkali cations, particularly in the V_r range of 0.2–1.0. However, the P values of the cesium ion (% P : 3.9–89.1) were higher than the P values of the sodium ion (% P : 1.1–54.0) and the potassium ion (% P : 1.2–38.6). Fig. 15 depicts the precipitation fractions of the non-radioactive species. Fig. 16 shows the precipitation fractions of the cesium and strontium ions.

The precipitation fractions of the non-radioactive and radioactive species from the simulated NCAW stream are presented in Tables 14 and 15 using both IPA and EA as precipitation agents. The precipitation of the phosphate and fluoride ions from the NCAW stream by both

Table 20

The 2-Suffix equation (Eq. (1)) representation of the cation and anion species from the simulated NCAW stream

Stream	Model's parameters		RMSE	%AAD	NP
	C_1^a	C_2^b			
Aluminum ion					
NCAW: IPA	-0.0499	-1.7004	0.0619	46.74	8
NCAW: EA	-1.1581	1.8334	0.1987	25.22	7
Sodium ion					
NCAW: IPA	-0.3105	0.6768	0.0295	24.39	7
NCAW: EA	-1.5384	0.7507	0.0714	11.64	6
Potassium ion					
NCAW: IPA	-0.2099	0.2767	0.0242	23.17	6
NCAW: EA	-1.3971	0.6161	0.0525	7.60	6
Cesium ion					
NCAW: IPA	-0.4230	0.2182	0.0170	8.26	6
NCAW: EA	-3.1217	4.3143	0.0814	9.19	5
Nitrite ion					
NCAW: IPA	-0.0570	-3.7410	0.0227	12.08	6
NCAW: EA	-1.9821	3.2628	0.0569	6.50	5
Nitrate ion					
NCAW: IPA	-0.0751	0.0706	0.0228	33.56	7
NCAW: EA	-2.1201	5.1552	0.0451	5.97	5
Sulfate ion					
NCAW: IPA	-0.3617	-5.4898	0.1249	15.38	7
NCAW: EA	-3.8335	1.8221	0.3366	15.08	6

^a $C_1 = \ln(x_{1,3}/x_{1,2})$.^b $C_2 = A_{32}$.

IPA and EA were very high (%*P*: reached 99.9). The *P* values of the sulfate ion (14,408 ppm) were increased with the increase in the amounts of IPA or EA (e.g. at V_r : 2.0; %*P*: 92.0 in the case of IPA, and 95.6 in the case of EA). The precipitation fractions of these critical anions by IPA and EA from the NCAW stream are shown in Fig. 17.

The significant presence of the hydroxide ion drastically suppresses the precipitation of aluminum, nitrate, nitrite, and alkali cations (sodium, potassium, and cesium). Thus, the *P* values of these species were significantly low. However, when EA was used as a precipitation agent with the NCAW stream (Table 15), the *P* values of aluminum, nitrate, nitrite, and alkali cations were higher than their *P* values using IPA as a precipitation solvent. This would indicate that EA is to some extent more effective in precipitating these species from the NCAW stream than IPA.

4.4. Recovery of the precipitation solvents (IPA and EA)

The practicality of the tested precipitation process depends on the capability of recovering the precipitation solvent. The physical properties of IPA and EA suggest ease of

Table 21

The 3-Suffix equation (Eq. (2)) representation of the cation species from the selected and tested anion groups of the simulated NCAW stream using IPA

System	Model's parameters			RMSE	%AAD	NP	$x_{1,2}$	$x_{1,3}$
	C_1^a	C_2^b	C_3^c					
Sodium ion								
Group 1	-1.7789	1.5378	0.5734	0.0137	3.15	6	4.75E-3	8.01E-4
Groups 1 and 2	-2.2840	8.5330	1.3950	0.0622	14.98	8	6.02E-3	6.13E-4
Groups 1 and 3	-4.2278	8.7011	4.9967	0.0070	4.29	7	9.97E-3	1.45E-4
Groups 1 and 4	-2.8060	7.8615	2.3178	0.0600	21.74	7	6.86E-3	4.15E-4
Groups 1 and 5	-3.3446	8.5187	3.9632	0.0248	15.46	8	1.23E-2	4.33E-4
Groups 1 and 6	-2.8534	5.1425	3.1695	0.0230	6.81	6	1.36E-2	7.85E-4
Groups 1-4	-3.1068	5.6581	1.9290	0.0185	5.01	8	1.29E-2	5.76E-4
Groups 1-6	-4.7200	12.681	5.2199	0.0636	10.04	6	2.82E-2	2.52E-4
Potassium ion								
Group 1	-2.1751	2.1393	0.8899	0.0113	7.42	6	2.03E-3	2.30E-4
Groups 1 and 2	-1.5750	2.8423	0.4436	0.0310	5.44	7	2.16E-3	4.47E-4
Groups 1 and 3	-3.0699	2.0762	2.0358	0.0105	9.83	7	2.16E-3	1.00E-4
Groups 1 and 4	-0.1428	-0.4446	-0.4907	0.0230	14.14	7	2.23E-3	1.93E-3
Groups 1 and 5	-2.1305	2.7324	1.2286	0.0188	13.28	8	2.16E-3	2.56E-4
Groups 1 and 6	-2.0399	2.3409	1.1938	0.0145	13.18	7	2.21E-3	2.88E-4
Groups 1-4	-1.4834	0.1316	0.3758	0.0328	15.44	8	2.16E-3	4.89E-4
Groups 1-6	-1.9682	2.1826	0.9401	0.0498	11.84	6	2.16E-3	3.01E-4
Cesium ion								
Group 1	-5.6467	2.4898	2.0728	0.0378	6.51	5	1.45E-5	5.12E-8
Groups 1 and 2	1.8431	-4.3999	-1.8579	0.0362	4.02	4	1.41E-5	8.90E-5
Groups 1 and 3	8.3971	-14.307	-0.5250	0.0226	4.30	4	1.64E-5	7.26E-2
Groups 1 and 4	-11.832	11.637	4.3751	0.0413	3.53	6	1.45E-5	1.05E-10
Groups 1 and 5	-15.478	179.99	64.640	0.0045	2.77	4	1.43E-5	2.71E-12
Groups 1 and 6	-11.030	6.5960	4.8373	0.0436	12.60	5	1.61E-5	2.61E-10
Groups 1-4	-4.8787	1.0798	1.7435	0.0377	9.71	5	1.36E-5	1.03E-7
Groups 1-6	8.0940	-11.051	-6.4407	0.0202	0.90	6	1.47E-5	4.81E-2

^a $C_1 = \ln(x_{1,3}/x_{1,2})$.

^b $C_2 = \Lambda_{32}$.

^c $C_3 = \Lambda_{23}$.

recovery. Tables 16 and 17 present, respectively, the recovery of IPA and EA from the NCAW stream, and de-ionized water. As shown in Tables 16 and 17, a substantial recovery of IPA (97.5–99.9%) and EA (94.2–99.5%) from the NCAW stream was achieved compared to moderate recovery from the de-ionized water (IPA: 46.7–94.4%; EA: 37.0–86.5%) using a simple vacuum system. This would suggest that the presence of inorganic species in the NCAW stream has appreciable positive effects on the relative volatility of IPA and EA, which enhances their separation from the aqueous phase. However, the recovery of IPA is higher than the recovery of EA. This is due to the low purity of EA (70% aqueous solution), which lowers the vapor pressure of EA from 760 to 450 mmHg at 20°C (vapor pressure of IPA is 478 mmHg at 20°C). It should be pointed out that the remaining concentrations (after applying vacuum) of IPA or EA in the de-ionized water were relatively identical. This may

Table 22

The 3-Suffix equation (Eq. (2)) representation of the anion species from the selected and tested anion groups of the simulated NCAW stream using IPA

System	Model's parameters			RMSE	%AAD	NP	$x_{1,2}$	$x_{1,3}$
	C_1^a	C_2^b	C_3^c					
Nitrate ion								
Group 1	-5.8614	12.383	5.8784	0.0154	4.66	8	3.08E-2	8.76E-5
Groups 1 and 2	-4.6411	9.7780	4.9343	0.0600	7.40	6	2.92E-2	2.82E-4
Groups 1 and 3	-3.6279	5.8726	4.0007	0.0139	8.18	8	2.92E-2	7.76E-4
Groups 1 and 4	-1.9602	0.2549	1.4662	0.0348	19.99	7	3.07E-2	4.32E-3
Groups 1 and 5	-1.0644	1.1258	0.1195	0.0319	5.30	6	3.38E-2	1.17E-2
Groups 1 and 6	-4.3992	8.9272	4.8439	0.0257	15.16	7	2.96E-2	3.63E-4
Groups 1-4	-4.2860	10.549	4.6006	0.0206	6.98	8	2.92E-2	4.02E-4
Groups 1-6	-4.2540	5.6181	4.0159	0.0398	8.41	8	3.15E-2	4.47E-4
Sulfate ion								
Groups 1 and 3	-22.527	38.603	20.527	0.2798	35.31	8	2.69E-3	4.44E-13
Groups 1-4	-19.442	37.302	16.615	0.3538	33.00	8	2.71E-3	9.76E-12
Groups 1-6	-27.627	54.703	23.520	0.4296	26.17	8	2.70E-3	2.71E-15

^a $C_1 = \ln(x_{1,3}/x_{1,2})$.

^b $C_2 = \Lambda_{32}$.

^c $C_3 = \Lambda_{23}$.

indicate that the removal of IPA or EA from de-ionized water is to some extent irrelevant to their initial concentrations before applying vacuum.

4.5. Evaluation of the solubility framework's equations

Regressions of the precipitation measurements were performed using the weighted least squares objective function (SS). A Marquardt nonlinear regression procedure was employed in the precipitation calculations [36]. The objective function, SS, used for the evaluation of the models equations is given as follows [23,25]:

$$SS = \sum_{i=1}^{NP} \left(\frac{Y_{Cal} - Y_{Exp}}{Y_{Exp}} \right)^2 \quad (10)$$

where Y_{Cal} is the calculated variable, and Y_{Exp} the experimental variable, and given as follows [23,25]:

$$Y = \ln(1 - P) \quad (11)$$

According to Eq. (10), the root mean square error (RMSE) provides an appropriate measure of the overall model performance for a given data set more so than the percentage average absolute deviation (%AAD) [23].

The acquired precipitation data on the: (1) nitrate group; (2) each of the binary groups that contains the groups of nitrate-phosphate, nitrate-sulfate, nitrate-fluoride, nitrate-nitrite, and nitrate-carbonate; (3) combined nitrate, phosphate, sulfate, and fluoride groups; (4)

Table 23

The 3-Suffix equation (Eq. (2)) representation of the cation and anion species from the simulated NCAW stream

Stream	Model's parameters			RMSE	%AAD	NP	$x_{1,2}$	$x_{1,3}$
	C_1^a	C_2^b	C_3^c					
Aluminum ion								
NCAW: IPA	-1.6034	4.8592	5.3053	0.0259	20.94	8	7.69E-3	1.55E-3
NCAW: EA	-5.6650	29.108	16.839	0.0463	8.77	7	7.69E-3	6.53E-5
Sodium ion								
NCAW: IPA	-0.9323	1.8774	1.1266	0.0135	7.80	7	8.30E-2	3.27E-2
NCAW: EA	-3.4951	4.2185	3.3888	0.0404	6.84	6	8.30E-2	2.52E-3
Potassium ion								
NCAW: IPA	-0.7282	1.1333	0.4517	0.0138	16.52	6	2.26E-3	1.09E-3
NCAW: EA	-2.4753	1.6555	1.0980	0.0330	5.70	6	2.26E-3	1.90E-4
Cesium ion								
NCAW: IPA	-0.4713	0.2607	0.0723	0.0178	8.25	6	9.94E-6	6.20E-6
NCAW: EA	-1.4913	2.8673	0.0309	0.0707	10.33	5	9.94E-6	2.24E-6
Nitrite ion								
NCAW: IPA	-0.2166	-3.2863	-0.3699	0.0231	13.24	6	6.89E-3	5.55E-3
NCAW: EA	-2.7304	5.1678	2.0481	0.0596	6.35	5	6.89E-3	4.50E-3
Nitrate ion								
NCAW: IPA	-0.3753	0.8029	0.4038	0.0105	22.53	7	2.94E-2	2.02E-2
NCAW: EA	-2.7310	6.7736	1.9406	0.0462	5.60	5	2.94E-2	1.92E-3
Sulfate ion								
NCAW: IPA	-6.3128	4.5637	4.7887	0.0226	2.79	7	2.68E-3	4.87E-6
NCAW: EA	-11.875	16.300	8.7932	0.0713	4.54	6	2.68E-3	1.87E-8

^a $C_1 = \ln(x_{1,3}/x_{1,2})$.^b $C_2 = \Lambda_{32}$.^c $C_3 = \Lambda_{23}$.

combined nitrate, phosphate, sulfate, fluoride, nitrite, and carbonate groups and (5) simulated NCAW stream were used to evaluate Eqs. (1) and (2). Tables 18–23 summarize the results of the tested Eqs. (1) and (2) for the studied systems. These tables include the regressed interaction parameters of the equations and complete evaluation statistics. However, species with very high precipitation fractions (e.g. phosphate, fluoride, calcium, strontium, and in some cases aluminum) were removed.

The 3-Suffix equation, Eq. (2), with four interaction parameters (including Λ_1) represents the ultimate correlative ability. Such a level of complexity may be excessive since the RMSE for the precipitation data using Eq. (2) without Λ_1 are mostly within the expected experimental uncertainty in the combined precipitation data sets used. The salt binary-solvent interaction parameter (Λ_1) in Eq. (2) is thus neglected.

As shown in Tables 18 and 20, Eq. (1), the 2-Suffix equation, with one solvent-solvent interaction parameter (Λ_{32}) provides, in most cases, acceptable correlation over the entire range of θ_3 . As given in Tables 21 and 23, however, substantial improvements in the predictive ability were achieved when the two solvent-solvent interaction parameters

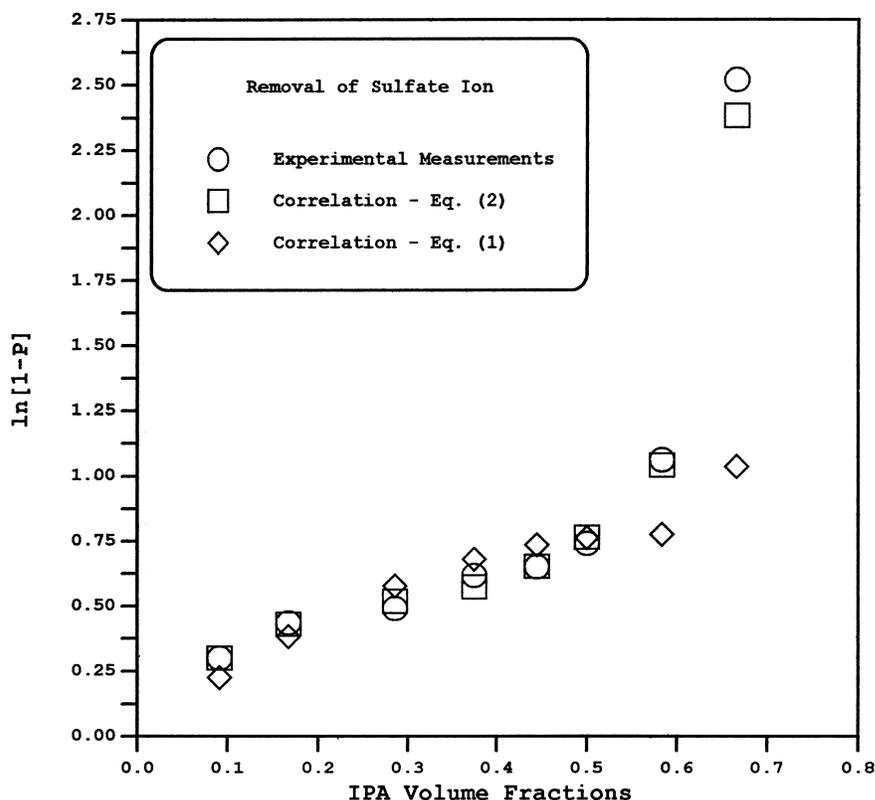


Fig. 18. Removal of the sulfate ion from the NCAW stream using IPA.

were employed by Eq. (2), the 3-Suffix equation. The improvement was attributed to the unsymmetric form of the solvent–solvent interaction parameters with respect to θ_3 . The combination of these two solvent–solvent interaction parameters (Λ_{32} and Λ_{23}) in Eq. (2) provides good correlation of the precipitation data.

As a demonstration case, Fig. 18 exhibits a plot of the left-hand side of Eq. (1) or Eq. (2) versus the IPA volume fraction (θ_3) for the precipitation of the sulfate ion from the NCAW stream (Table 14). Without the addition of IPA, the left-hand side of these equations is zero since there is no precipitation ($P = 0$). However, without the use of the solvent–solvent interaction parameters (Λ_{32} and/or Λ_{23}), the precipitation measurements can be fit to some extent with a straight line. This situation is equivalent to the ideal mixture solubility based on Henry's law. To extend the model fitting to the maximum value of θ_3 , the interaction parameters were needed to account for the non-ideality of the system. Eq. (1) with one regressed solvent–solvent interaction parameter (Λ_{32}) was somewhat insufficient in correlating the precipitation of the sulfate ion over the entire range of θ_3 (RMSE = 0.1249; %AAD = 15.4). However, significant improvement in the correlation ability was achieved when the two regressed solvent–solvent interaction parameters were

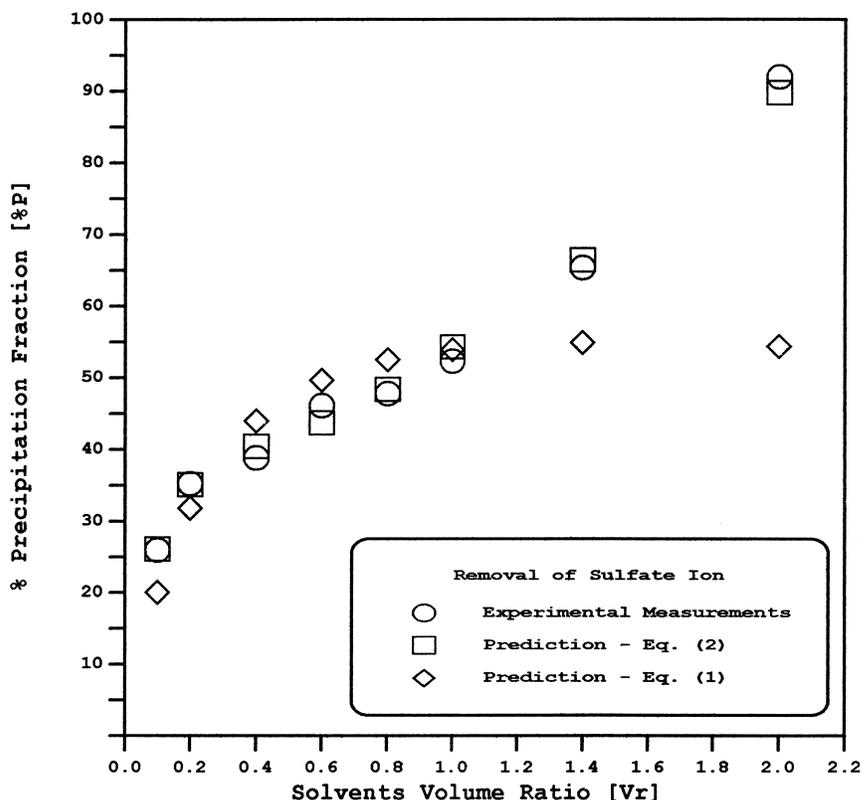


Fig. 19. Experimental and predicted precipitation fractions of the sulfate ion from the NCAW stream using IPA.

employed by Eq. (2) (RMSE = 0.0226; %AAD = 2.8). Fig. 19 shows the experimental precipitation fractions of the sulfate ion from the NCAW stream using IPA as a precipitation solvent at different V_r values, as well as the predicted precipitation fractions by Eqs. (1) and (2).

The produced optimum interaction parameters can be used to estimate the precipitation fractions (% P) of the studied species systems, for instance: (1) at different concentration levels of a targeted inorganic species; or (2) in different waste streams with similar or approximate abundance of major and minor species; or (3) at different solvents volume ratio (V_r) where no experimental data are available. This would provide economy of experimental efforts and cost savings.

As discussed in the precipitation concept section, several factors would determine the suitability of a selected organic solvent for the precipitation process. One of the most important factors in selecting the organic solvent is the solubility of the targeted inorganic species in the selected solvent [23]. Tables 21 and 23 present the estimated solubilities of tested species in the precipitation solvent ($x_{1,3}$) using the interaction parameter (C_1) of Eq. (2), the optimum predictive case. The solubility of an inorganic species in a simple

organic solvent is typically orders of magnitude less than its aqueous solubility [37]. It appears that the Eq. (2), is capable of predicting the expected trend of the solubilities of the tested inorganic species in the precipitation solvents. No experimental data are available to draw a conclusion regarding the reliability of the estimated values. However, more fundamental and experimental work is needed to study the solubilities of targeted inorganic species individually in the precipitation solvents.

5. Conclusions

As indicated by the preliminary data, the precipitation concept can potentially be employed for the pretreatment of both sludge and supernate. In the case of acid-dissolved sludge and acidified supernate where the anions are limited to nitrate, fluoride, chloride, phosphate and sulfate (no hydroxide), the concept can effectively be used to process such waste streams. The removal of polyvalent cations as well as the critical anions species are very significant. However, the process should be carefully optimized for selective removal of the radioactive species from the bulk of the cations.

Gel formation is one of the biggest problems associated with acid-dissolved sludge with nitric acid (e.g. gel formation prevents mixing, prevents pumping, retards separation, coats surfaces, and clogs filters). In contrast, no gels will be formed with caustic leaching. In the case of alkaline-dissolved sludge, the concept can be used in conjunction with the current “caustic leaching” sludge pretreatment methods such as the “enhanced sludge washing” (ESW) method (see [38]). However, careful optimization of the ESW needs to be exercised to minimize the amount of sodium hydroxide required.

In the case of alkaline supernate, the concept can be used as a stand alone process to primarily target radioactive alkaline cations (e.g. strontium) and key non-radioactive species such as phosphate, fluoride, and sulfate ions. Another possible scheme for alkaline supernate, which is aimed at removing aluminum ion effectively, is to employ the precipitation concept in conjunction with the “caustic recycle process” (CRP) [39]. The CRP is an electrochemical-based process to remove sodium hydroxide from waste streams. The removal of the hydroxide ion by the CRP process will facilitate effective separation of the aluminum ion by the proposed precipitation process.

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