

Potentiality of sodium metabisulphite for the selective iron removal prior to uranium elution from its loaded anion exchange resin

Mohamed S.Nagar

Nuclear Material Authority, 530 p.o Box Maadi, Cairo, (EGYPT)

E-mail: mf_nagar@yahoo.com

ABSTRACT

Most uranium was include ferric iron to varying degrees in a manner that recovery of the former from its sulphate leach liquors by anion exchange resin would be contaminated with some anionic ferric complexes. In order to avoid iron removal from uranium eluate the effective reductant sodium metabisulphite (SMBS) has been applied to remove the co-adsorbed (captured) iron prior to uranium elution. Both batch equilibrium testing using synthetic solutions and column studies upon Gattar leach liquor has been achieved using the Chinese anion exchange resin (B263D). It was found the iron contaminating the resin is not adsorbed but is mainly occupying the resin pores. By using (SMBS), it was possible in the synthetic solution batch studies to selectively remove 99% of the iron from the resin while the co-eluted uranium did not exceed 0.5%.

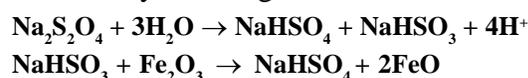
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INTRODUCTION

Iron is a widespread element where in the earth's crust, its average assay attains up to 5% besides its presence in soil as well as in surface and ground water. This widespread distribution leads to its interference in several hydrometallurgical ore processing or analytical procedures of several elements. On the other hand, uranium is ubiquitously present in the environment and forms part of the nuclear fuel cycle and its determination in various matrices is quite essential whether during prospecting and processing up to waste management and protection of environment.

In these cases and apart from other metal impurities, iron would interface to a large extent and its separation has become quite essential. According to Pulhani, et al^[1] for example presence of large quantity of uranium and iron causes reduction in the efficiency of laser fluorometric determination of ura-

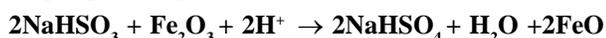
nium due to quenching effects. While the classical methods of iron separation from uranium including element exhaustion, ion exchange or co-precipitation have proved inefficient, these authors have been able to devise a two-stage procedure for this separation in ground water samples using anion exchange resin in 0.025 M H₂SO₄ acid. In the meantime, Irwin has eliminated the iron rust stains FeO₃.H₂O (or FeO.OH) from paper by first reducing the ferric ions into the soluble ferrous ion followed by its sequestering in water by adding a chelating agent such as EDTA^[2]. Sodium dithionite or sodium byrosulphite (Na₂S₂O₄) has been proven to be effective for rust removal by reducing the ferric ions as follows^[3] :



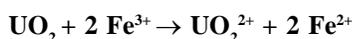
However, sodium dithionite presents actually significant practical problems as it is extremely flammable and prone to spontaneous combustion. On the other hand, sodium metabisulphite (Na₂S₂O₅) is not

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flammable and is far less expensive than sodium dithionite^[4]. Its reducing reaction for ferric ion can be represented as follows:



In the acid leach liquor of uranium ores, iron is generally present in varying amounts according to the decomposition and acid concentration. While ferric iron is capable of oxidizing the insoluble tetravalent uranium that might be present in the ore to the soluble hexavalent state.



According to, the leached uranium would exist in its hexavalent state within the emf of 400 to 500 mV at which a major part of iron is present in its ferric state. In this regard, it has to be indicated that ferric iron can form anionic complexes which compete with uranium for resin sites when its recovery from acid leach liquors using anion exchange resin. The type of these soluble complexes involve $[\text{Fe}(\text{SO}_4)_n]^{3-2n}$ or $[\text{Fe}(\text{OH})(\text{SO}_4)_2]^{-2}$ and this formation tend to increase in concentration with increasing of pH at a faster rate than do the uranyl complexes^[5]. In the meantime, iron is also often present in concentration considerably higher than uranium and will accordingly compete with it for the exchange sites.

Presence of iron in the uranium leach liquor obtained by heap leaching of Gattar uranium occurrence (Eastern Desert of Egypt), has actually presented a number of problems when recovering the latter by the chosen anion exchange resin (B236D). Thus the uranium eluate would be contaminated with ferric ions due to its co-adsorption upon the resin besides decreasing the uranium saturation capacity of resin. Formation of the ferric iron anionic complexes can be decreased by working at pH values less than 1.8^[6]. Trails to precipitate the co-eluted iron at pH 3.5 prior uranium precipitation was unsuccessful due to significant occlusion of uranium in the precipitate. The present work has thus been oriented towards prior elimination of iron by its selective elution from the loaded resin i.e a procedure

that could be described as a tow steps elution. For this purpose, sodium metabisulphite would be applied as a selective iron eluent in the present work of treating Gattar leach liquor.

EXPERIMENTAL

Materials

Resin characteristics

The strong base anionic exchange resin (D263B) imported from China, (of a density of 0.7g/ml and particle size of 0.55 mm) has been used in the present work. This resin is highly selective for uranium at pH values ranging from 1.5 to 1.9^[7]. where the theoretical capacity of 60mg U/g dry resin has been reported. The resin column was pretreated with three-bed volume of 0.3M H_2SO_4 solution and then washed with deionized water until the effluent contained no chloride ion.

Synthetic solutions

An aqueous ferric iron solution assaying 2g/l was prepared by dissolving 7.1g ferric sulphate $\text{Fe}_2(\text{SO}_4)_3$, reagent grade, in 1.0 L of acidified water. Also, a stock uranium solution assaying 2 g/l was prepared by dissolving 3.52g of $\text{UO}_2(\text{SO}_4) \cdot 3\text{H}_2\text{O}$ in 1.0 L of deionized water.

Gattar leach solution

The applied working leach liquor used in this study was provided from Gattar experimental mini pilot plant unit. The latter was found to assay 0.5 g U/L, 2g/l iron and its pH was found to attain 1.8.

Experimental procedures

Two experimental procedures have actually been used in the present work. These included the batch technique in which the prepared U/Fe solution was applied to investigate the relevant factors while the column procedure was applied upon the provided Gattar leach liquor.

Batch treatment

Batch adsorption experiments were performed by shaking 20g samples of the working anion exchange resin (D263B) with 4.0 litres of the synthetic

solution at pH 1.8 using a magnetic stirrer for 1.0 hour. The adsorbed amounts of uranium and iron were calculated by analyzing their remaining values in the treated solution.

For elution or de-sorption of the loaded uranium from the resin samples, the latter was firstly washed with a sulfuric acid solution having the same molarity of the working liquor. This was then followed by dividing the resin into two halves; the first half was eluted by 1.0M NaCl acidified to 0.1M H₂SO₄ acid and the second half was first eluted by Na₂S₂O₅ to remove iron followed by washing with water then uranium was eluted by the prepared eluate 1.0M NaCl / 0.1M H₂SO₄ solution. The latter experiment was repeated to determine both the optimum contact time and the sodium metabisulphite concentration.

Column treatment

A 15 ml bed volume of the working anion exchange resin (D263B) in its chloride form and packed in a glass column of 1.2 cm diameter and 30 cm height was used for the treatment of the provided Gattar pregnant solution (0.5g/L uranium, 20g/L SO₄²⁻ and 2.0g/L iron). After adjusting the pH to 1.8; the solution was passed through the resin bed till saturation at a flow rate of 2.0ml / min and the effluent was collected in 50 ml fractions and chemically analyzed for uranium and iron.

For uranium elution; the resin bed was given a backwash step with water to displace the feed solution from the column and to loosen and expand the bed to wash off any accumulated fine solids. The resin was then allowed to settle and an eluant was passed down the column to displace the ferric iron by firstly reducing it to the ferrous state and removing it before the final uranium elution step. The most commonly used eluants consist of 0.025N H₂SO₄ acid then with (0.045M Na₂S₂O₅ / 0.1M H₂SO₄) for iron (ferrous form) removal and finally followed by 1.0M sodium chloride acidified to 0.1M by sulphuric acid for uranium elution.

Analytical procedures

Uranium analysis

Uranium content in all the working solution streams was analyzed either by the redox titrimetry

following Davies and Gray method in high concentration^[8] or Arsenazo III used as described in the method of Marczenko^[9] to determine the uranium in the different aqueous phases. Absorbance of the formed uranium Arsenazo III complex was measured at 650 nm against proper standard solutions using a Lambda3 UV/VIS spectrophotometer (Perkin-Elmer, USA).

Iron analysis

The iron concentration (as Fe₂O₃) in all the working stream solutions was determined using the EDTA procedure. Thus, to 5 ml of each sample solution, 1ml of the sulfosalicylic acid indicator (0.2g/100 ml distilled water) was added before adjusting the pH to 2.5, then titration against 0.01 M EDTA solution was carried out until the disappearance of the solution color^[9].

RESULTS AND DISCUSSION

Batch treatment of the synthetic U/Fe solution

Adsorption and normal elution

A 20 g sample of the working Chinese resin was shaken with 4.0 L of the synthetic sulphate U/Fe solution (0.4g/L uranium and 2.0g/L iron at pH 1.8) for 1.0 hour contact time in each cycle. From the obtained results shown in TABLE (1) for 8 adsorption cycles, it was found that uranium adsorption has gradually been decreased till almost resin saturation at which 1.08g uranium is adsorbed equivalent to 90% of the theoretical resin capacity (60 mgU/g resin). This decrease in capacity is due to the co-adsorption of the anionic iron sulphate complex in a manner to occupy 10% of the exchange site of the resin. However the amount of the adsorbed iron shown in TABLE (1) attains up to 2.86g equivalent to about 433mg/g resin is far exceeding the exchange site and is actually found in the pore site of the working resin sample. On the other hand, it has to be mentioned that in spite of the resin selectivity for uranium, the fact that the iron content in most leach liquors is far exceeding the uranium content, it would therefore occupy most of the exchange sites in early adsorption stages. Further contact with the leach li-

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TABLE 1 : Adsorption of uranium and iron from the synthetic solution on the Chinese D236B anion exchange resin

Cycle No (500ml/cycle)	U distribution		Fe distribution	
	Filtrate,ppm	Loaded, g	Filtrate,ppm	Loaded, g
1	0.0	0.20	250	0.875
2	0.0	0.20	400	0.800
3	20	0.19	550	0.725
4	60	0.17	970	0.515
5	110	0.145	1600	0.200
6	190	0.115	2000	0.00
7	300	0.050	2000	0.00
8	380	0.01	2500	0.25 desorbed
Total Vol= 4000		1.08g		2.86g

TABLE 2 : Uranium normal elution of the loaded resin sample by 1.0M NaCl / 0.1 M H₂SO₄ eluant

Cycle No (150ml/cycle)	U eluted, %	Iron removal, %
1	24.7	50.0
2	45.7	30.0
3	11.4	12.0
4	3.8	4.0
Total	85.6%	96.0%

quor would result in partial displacing the early adsorbed iron complex species by the uranium anionic species.

For uranium elution from the loaded resin, the conventional eluent of 1.0M NaCl acidified to 0.1M with sulphuric acid has been used in 4 successive cycles of 150 ml each for a contact time of 1.0 hour. The obtained results are that given in TABLE (2) indicate that both uranium and iron are removed together. Thus, while about 25% of the loaded uranium was eluted in the first cycle, it has however been accompanied by 50% of the loaded iron. In the next elution cycle, the obtained uranium amounted to about 50% but its contaminated with 30% of the loaded iron. After the 4th elution cycle, the total uranium eluted has attained about 86% but its mixed however with 96% of the loaded iron in a manner to greatly exceed that of uranium. Consequently, the latter should first be separately removed prior to uranium precipitation from the obtained eluate in order not to contaminate the final uranium product (yellow cake). For this purpose, iron should first be removed by its alkali precipitation at pH of about 3.5. In this case, it was repeatedly shown that a relatively high uranium amount ranging from about

10 to 30% would be co-precipitated.

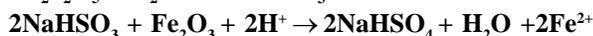
Potentiality of selective iron removal

In order to obtain an almost pure uranium eluate from the loaded resin, it was found necessary to selectively remove the iron prior to uranium elution. According to the above mentioned previous works^[1,2], it was indicated that iron can indeed be selectively removed through its reduction using suitable reductants; namely sodium dithionite Na₂S₂O₄ or the sodium bisulphite which is commonly referred to as sodium metabisulphite (Na₂S₂O₅). The latter is actually preferred since the duration of effectiveness of the former is usually in the range of few hours only^[3]. In addition, Na₂S₂O₅ (SMBS) is not flammable and does not require hazardous materials freight besides being far less expensive than sodium dithionite^[4]. Chemically when the SMBS reagent is dissolved in water, it dissociates into two molecules of sodium bisulphite (NaHSO₃) during which, a small amount of SO₂ is released and which would release some H⁺ ions after its water dissolution to give the sulphurous acid (H₂SO₃). Accordingly, the adsorbed or captured ferric iron would be reduced to Fe²⁺ which is easily washed off the resin by water^[10]. These reactions can be summarized as fol-

TABLE 3 : Elution results of U/Fe from the loaded D263B anion exchange resin using different eluants

Reagents	U eluted%	Iron removal %
0.1M H ₂ SO ₄	10	55
0.13 M Na ₂ S ₂ O ₄ / 0.1M H ₂ SO ₄	15	85
0.11 M Na ₂ S ₂ O ₅ / 0.1M H ₂ SO ₄	0.5	99
1.0M NaCl / 0.1M H ₂ SO ₄	90.4	85

lows:



To realize this objective, 5 g sample portion of the working Chinese resin (D263B) that have been loaded from the prepared U/Fe synthetic solution were shaken for 1 hour with 150 ml of 4 different eluant solutions. The latter involved 0.1M H₂SO₄, 0.13M Na₂S₂O₄, 0.11M Na₂S₂O₅ or 1.0M NaCl being acidified to 0.1M with sulphuric acid. From the obtained uranium and iron elution efficiencies give in TABLE(3), it is clearly evident that the acidified SMBS solution has achieved 99% iron removal accompanied with only 0.5 % uranium. Subsequently, uranium can then be eluted with its normal eluant mixture (1M NaCl / 0.1MH₂SO₄).

Optimization of the relevant factors for iron removal

Effect of sodium metabisulphite concentration

To study the effect of SMBS concentration, a series of experiments were carried out by shaking 20g sample portions of the anion exchange resin D263B loaded by 1.08g uranium and 2.86g iron with 150 ml of different concentrations of SMBS solution ranging from 0.01 to 0.08M at room temperature for 1.0 hour. The obtained results shown in Figure (1) reveal that iron removal has steadily increased with increasing the SMBS concentration till reaching a maximum removal exceeding about 98% at 0.045M of SMBS acidified to 0.1M H₂SO₄.

Effect of contact time

A series of experiments were carried out using the same amount of the working anion exchange resin (D236B) loaded by 1.08g of uranium and 2.86g of iron were shaken with 150 ml of 0.045M sodium metabisulphite (SMBS) acidified to 0.1M H₂SO₄ at different contact time periods ranging from 10 to 100

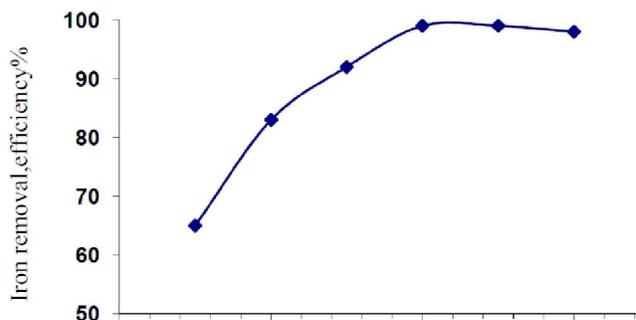


Figure 1 : Effect of SMBS concentration on selective iron removal efficiency

min. The obtained results shown in Figure (2) reveal that the maximum iron removal exceeding about 98% removal was obtained at a contact time of about one hour.

The determined optimum values of SMBS concentration and contact time have been applied on a loaded resin sample to selectively separate the adsorbed and captured ferric iron leaving uranium to be subsequently eluted by its normal eluant (1.0M NaCl / 0.1M H₂SO₄). For iron removal, the 20g loaded resin sample was subjected to 3 treatment cycles using 0.045M SMBS solution for 1.0 hour shaking time in each cycle. The obtained results given in TABLE (4) indicate that iron removal has attained 83,15 and 1% in the 3 cycles i.e. a total of 99% iron removal while uranium has completely been unaffected. The latter was then subjected to elution using 150 ml of its normal eluant (1.0M NaCl / 0.1M H₂SO₄) for 4 cycles each using a contact time of 1.0 hour. TABLE (5) shows the stepwise elution results where the elution efficiency attained 41.4, 31.4, 14.3 and 4.7 % in the 4 cycles amounting to 91.1% uranium elution efficiency.

Column treatment of Gattar leach liquor

Column adsorption of Gattar leach solution

The prepared anion exchange resin (D236B) column (15 ml wsr in a glass column of 1.2 cm di-

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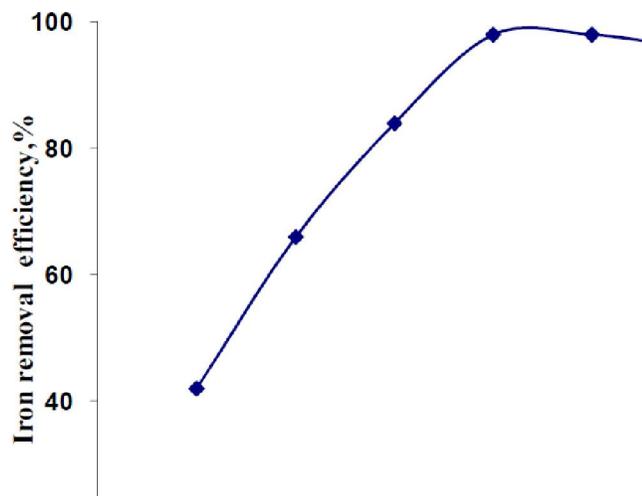


Figure 2 : Effect of contact time on selective iron removal efficiency

TABLE 4 : Iron removal from loaded resin by 0.045M $\text{Na}_2\text{S}_2\text{O}_5$ / 0.1M H_2SO_4

Cycle No (50ml/cycle)	U eluted, %	Iron removal %
1	0.0	83
2	0.0	15
3	0.0	1.0
Total	0.0	99%

ameter) was loaded with 1.5 liters of the provided Gattar sulphate leach liquor (0.5g/L uranium and 2.0g/L iron at pH 1.8) at a contact time of 3 min equivalent to a flow rate of 2 ml/min.

From the obtained adsorption data plotted in Figure (3), it was shown that while iron has ceased adsorption after the 4th influent sample (saturation level), uranium has ceased its adsorption at the 6th influent sample (saturation level). Proper calculation has thus indicated that the saturation point was reached at approximately 1500 ml for uranium (0.45g loaded) and 1000 ml for iron (1.05g loaded).

Direct elution of uranium and iron from the loaded resin column

Higher amount of adsorbed (captured) Fe reduced the exchange of uranium on the anion exchange resin and more uranium was eluted along with iron. In this case, the separation can be possibly improved with more bed volume of the resin.

Figure (4) gives the recovery of uranium spiked (0.396 U) along with 0.88g of iron from loaded resin using (1.0M NaCl / 0.1 M H_2SO_4). The recovery

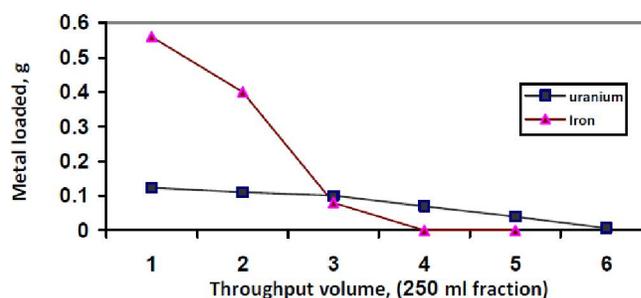


Figure 3 : Gradual uranium and iron adsorption from Gattar leach liquor upon the Chinese anion exchange resin column

TABLE 5 : Successive batch elution of uranium from the loaded resin sample after iron removal by its normal eluant (1.0M NaCl / 0.1 M H_2SO_4)

Cycle No (150ml/cycle)	U eluted%
1	41.4
2	31.4
3	14.3
4	4.70
Total	91.1

varied from 88.0 to 90% for uranium and 84% for iron.

Successive iron and uranium elution from the loaded resin column

Selective iron elution from the loaded resin column

In the alternate procedure, the above U/Fe loaded resin column was then subjected to selective iron removal using 0.045M of SMBS / 0.1M H_2SO_4 solution at a flow rate of 1.0 ml /min. The eluate fractions were collected every 10 ml for iron and uranium analysis. From the concentration of iron and uranium in the collected eluate fractions every 10 ml, the eluted iron and uranium amount were calculated and plotted in Figure (5). From the latter, it has been shown that most of the adsorbed (captured) iron (94.2%) was removed with 60 ml of the eluant. While uranium is absent in the first 50 ml throughput volume, it started to show up in the 6th fraction.

Uranium elution from the loaded resin column after iron removal

In the second step, 180 mL of the normal eluant mixture (1.0M NaCl / 0.1M H_2SO_4) has been able in six fraction (30ml) to selectively elute the

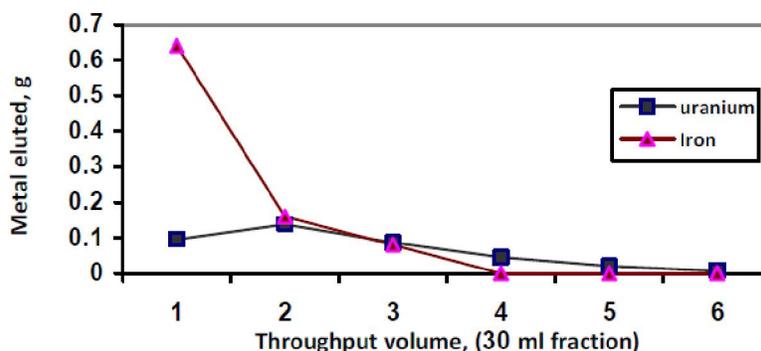


Figure 4 : Direct elution of uranium and iron from the loaded resin column by (1.0M NaCl / 0.1 M H₂SO₄)

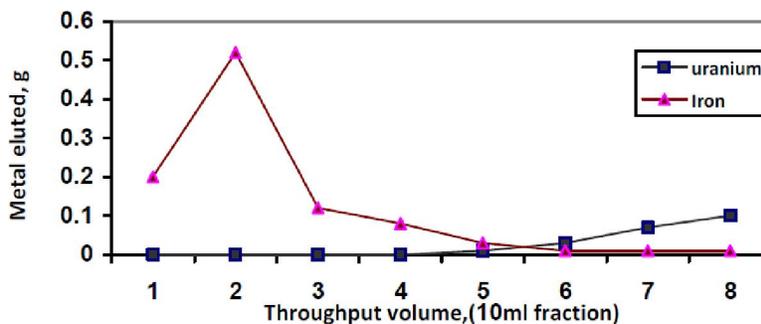


Figure 5 : Selective iron elution from the loaded resin column using SMBS

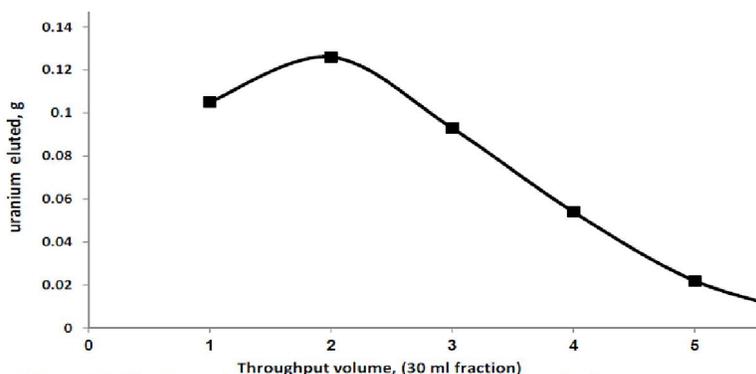


Figure 6 : Uranium elution from the loaded resin column after iron

adsorbed uranium content (0.45g). Figure (6) shows the successive stages of eluted uranium. From the latter, it was found that 90.4% of the loaded uranium has been recovered after the prior removal of 94.2% of the adsorbed (captured) iron by the SMBS eluant.

CONCLUSION

Sodium metabisulphite (SMBS) acidified with sulphuric acid has proven quite effective in selective iron removal from the uranium loaded anion exchange resin. Applying the studied eluant composition (0.045M SMBS/0.1M H₂SO₄) upon the working anion exchange resin after U/Fe loaded by Gattar

leach liquor, it was possible to selectively elute most of iron (92.5%) before effective elution. The latter was then almost selectively eluted to extent of 90.4% by applying its normal eluant (1.0 M NaCl/ 0.1M H₂SO₄).

ACKNOWLEDGMENTS

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