Recovery of uranium from low concentration leach liquor of acid in-situ leaching

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Abstract. For problems of environment protection and cost in uranium recycle, the process flows of ion exchange and Eluex, which recovered uranium from low concentration leach liquor of acid in-situ leaching, were studied. Although the flow sheet of ion exchange process was simple, the Eluex process had an advantage over it due to large quantity of effluent and high processing cost in ion exchange process by comparative studies.

1. Introduction
In northern China, because of low uranium amount per square meter, uranium grade is generally lower (uranium grade is around 0.01%). The surrounding rock has good permeability (permeability coefficient is from 7 m/d to 10 m/d) and low content of carbonate. The process of acid in-situ leaching was employed in this ore block. However, the concentration of uranium in the leach liquor was low (15-30 mg/L). So the difficult problem, which concentrated uranium from low concentration solution, should be urgent to be resolved.

To get the high quality of uranium precipitation product and reduce the consumption of NaOH during the process of hydrometallurgy, ion exchange process and Eluex process had been employed to recovery uranium from acid in-situ leaching solutions. Comparisons of technique, economy and environmental protection between these two methods showed that Eluex process is more suitable for uranium recovery from the low concentration leach liquor in acid in-situ leaching. Finally, the comparatively good process and parameters were determined, and the ideal effect was acquired too.

2. Ion exchange process
Ion exchange process [1-4] is the main technology used in recovery of uranium from in-situ leaching solution, and it generally includes procedures of uranium adsorption from leach liquor, uranium elution from saturation resin and resin transformation. In China, the process of adsorption with fixed bed and elution with moving bed is employed by many uranium milling plants. However, this method usually causes the problems of high cost and environmental protection. In this study, only adsorption and elution process of fixed bed was discussed.

The pH value of the acid leaching solution is 1.62 and ORP is 315mV. The concentrations of U, Ca2+, Mg2+, Fe2+, Al3+, SO42- and Cl- were 22,465,413,480,277,8453 and 488mg/L respectively. Strong base anionic resin named D1 was used as adsorption material. The adsorption with three columns in series, which are fixed beds, is employed. And feeding mode is upward. Adsorption temperature is
from 10 to 20 °C with contact time 6 minutes. When uranium concentration of leach liquor was 20-30 mg/L, uranium saturation capacity of resin is 11-15 mg/mL, the breakthrough volume is about 600 bed volumes, and the ratio of saturation volume and breakthrough volume is about 1.5.

The acidic NaCl solution is employed to elute U from the saturation resin in a single fixed bed column. The eluent solution contains 90 g/L of NaCl and 5 g/L of H2SO4. The elution contact time is about 45-60 minutes. When the bed volume of eluate reaches to 9, the uranium concentration of eluate can drop to 50 mg/L. If the bed volume of eluate reaches to 3, the uranium concentration of eluate is highest. The OK liquor can be obtained from the 2nd to 5th BV. When uranium concentration in leach liquor is 25-30 mg/L, the saturation U capacity of resin is 10-13 mg/mL. Uranium concentration in the OK liquor can be maintained between 4.5 to 5.5 g/L, while the average consumption of NaCl is about 4.63 t/(t·U) and the elution rate is higher than 97%.

After elution of uranium loaded resin, the barren resin will be converted to Cl type. So it is necessary to convert the resin from the chloride form to the sulfate form before returned to the adsorption cycle. After uranium adsorption, effluent contains 8-10 g/L of SO42-, which can be used to convert the resin.

The conversion results show that at early stage of the transformation (0.25-0.5 BV), Cl- concentration in the liquor is relatively high and such liquor can be used for elution. In the next 5 BV of transformation solution, Cl- concentration becomes low enough to discharge into evaporation pond to prevent Cl- from accumulation in the leaching system.

The primary product of yellow cake is precipitated by the method of circulation aging from OK liquor. The precipitation reagent NaOH is put slowly into the OK liquor, and the pH value is adjusted to 7.0-7.5. The agitation is carried for 20-30 minutes, and the time of settlement aging is 12 hours. After multi-precipitations, the alkali consumption of 1 ton uranium product is relatively high. The average amount of alkali is 1.33 t, while the U concentration in the mother liquor is about 5 mg/L.

3. Eluex process

The Eluex process is a combined technology which makes the processes of ion exchange and solvent extraction to link together. Firstly uranium is extracted by the process of ion exchange from leach liquor, and then the saturation resin is eluted by sulfuric acid. Secondly the uranium is extracted by the process of solvent extraction from the acidic eluate, and then uranium and sulfuric acid are separated from each other. Finally, the uranium is concentrated at high magnification.

The uranium is extracted by process of ion exchange from leach liquor, and the saturation resin is eluted by 100 g/L of sulfuric acid. Under the condition of contact time with 40 minutes, uranium content of barren resin is less than 0.1 mg/(ml·wtr), and uranium concentration of effluent is less than 0.1mg/ml after 9 BV of elution. Uranium concentration of OK liquor is 2.4g/L.

During the procedure of sulfuric acid elution, the anionic uranium complexes in the resin are displaced by the rule of mass action due to high concentration of anionic bisulfate in eluent. The complexes of UO2(SO4)2-, and UO2(SO4)3+ in the eluate are dissociated partly, and the resultants of UO2SO4 and UO22+, which are not easy to be adsorbed by the resin with HSO4 type, are formed. Elution rate is dependent on the concentrations of exchangeable anion and diffusion of two kinds of exchanging anion due to simplicity of mass action. So the longer contact time and large amount of eluents are needed during the elution.

As feed solution of solvent extraction [5-7], the OK liquor of elution is extracted by the organic phase of 5% P204, 10% TBP and sulphonated kerosene. The size of the mixing chamber of mixer-settler is 1m×1m×1.5m. The side ratio of the mixing chamber and settler chamber is 1:3. The flow ratio of organic phase and aqueous phase is 1:2.1:4. The operating temperature is 18°C. After 4 stages of countercurrent extraction, the uranium concentration in the organic phase can reach to about 6g/L, and the uranium concentration in the raffinate is below 0.01g/L.

The loaded organic phase was handled by 2 stages of scrubbing and 3 stages of stripping. The flow ratio of organic phase and aqueous phase containing 110g/L of Na2CO3 in scrubbing process was 10:1, and the flow ratio of organic phase and aqueous phase in stripping process is 5:1-7:1. The operating
temperature is 20°C. Stripping results indicated that under the condition of 6 g/L of uranium concentration in loaded organic phase, the uranium concentration of OK liquor can reach to 50 g/L by 3 stages of stripping.

4. Comparison of 2 processes

4.1. Process flow
Compared with the processes of ion exchange and Eluex, the procedure of solvent extraction is increased in the Eluex process, which is more complicated.

4.2. Comparison of environmental benefit
4.2.1. Effluent quantity of acidic NaCl elution process
1) Effluent of resin transformation
To avoid the accumulation of Cl\(^{-}\) in leach solution, the amount of transformation effluent is totally 5 BV. If it is calculated by the 12 mg/mL of saturation capacity, the effluent quantity is 417 m\(^3\)/t U.
2) Effluent quantity of discharged sodium sulfate
Generally, the production capacity of sodium sulphate is 3.9 t/U in the process of acidic NaCl elution. Assuming that the solution will be discharged by precipitation of the mother liquor when the concentration of Na\(_2\)SO\(_4\) is 100 g/L, the effluent quantity is 39 m\(^3\)/t U.

4.2.2. Effluent quantity in eluex process
1) Raffinate discharge
The barren organic phase contains Na\(^+\), of which 5% P2O4. The concentration of Na is around 0.149 mol/L. The Na\(^+\) enters into aqueous phase by exchanging with UO\(_2^+\) and H\(^+\) during extraction process and then sodium sulphate is produced. Uranium capacity of saturated organic phase during Eluex process is 6.16 g/L, therefore, the yield of sodium sulphate is 1.74 t Na\(_2\)SO\(_4\)/t U. Assuming that the solution will be discharged when the concentration of sodium sulphate reaches to 100 g/L, the effluent quantity is 17.4 m\(^3\)/t U.
2) Effluent quantity of discharged sodium carbonate
During the recirculation of stripping feed solution in the preparation procedure of mother liquor, sodium carbonate will be accumulated by the addition of sodium bicarbonate. If the amount of sodium bicarbonate is 0.21 t NaHCO\(_3\)/t U, then the accumulation amount of sodium carbonate is 0.26 t Na\(_2\)CO\(_3\)/t U. Assuming that the concentration of sodium carbonate is 110 g/L, the effluent quantity of discharged carbonate discharge is 19.8 m\(^3\)/t U.

The effluent quantity in ion exchange process is much more than that in Eluex process, which is 456 m\(^3\)/t U compared with 19.8 m\(^3\)/t U in total. By utilization of Eluex process, the effluent quantity is reduced by above 95% of it.

4.3. Comparison of reagent cost
4.3.1. Reagent consumption of ion exchange process. The primary reagent consumption includes sulphuric acid, sodium hydroxide and sodium chloride.
1) The consumption of H\(_2\)SO\(_4\)
The sulfuric acid concentration in the eluent is 5 g/L. In the condition that the uranium concentration is 5 g/L, the theoretical acid consumption is 1 t H\(_2\)SO\(_4\)/t U.
2) The consumption of NaOH
The consumption of sodium hydroxide occurs in the procedure of precipitation, includes neutralization of sulphuric acid and precipitation of uranium. The actual average consumption is 1.33 t NaOH/t U.
3) The consumption of NaCl
The reason why sodium chloride consumes during production is that transformation solution and effluent of sodium sulphate are discharged. The actual average consumption is 4.63 t NaCl/t U.

4.3.2. Reagent consumption in Eluex process. The primary reagent consumption in this process consists of the inorganic and organic reagent. The inorganic reagent includes sulphuric acid, sodium
hydroxide and sodium bicarbonate, and organic reagent includes P204, TBP and kerosene, etc.
1) The consumption of $H_2SO_4$
The primary consumption of sulphuric acid occurs in the elution and extraction process. During the elution process, the decreasing portion of sulphuric acid enters the barren resin, and then it is returned to absorption process, and recycles in the process of in-situ leaching, which has no acid consumption. The sulphuric acid consumption in extraction is 0.38t $H_2SO_4$/t U.

2) The consumption of organic reagent
The primary consumption of organic reagent occurs in the extraction process. If the dissolution loss of organic phase is calculated after oil removal, the concentration of organic phase in the raffinate is less than 20mg/L and about 15% loss. The consumption of organic reagent is 0.66kg/t U.

3) The consumption of NaHCO₃ and Na₂CO₃
In stripping process, besides sodium carbonate consumption in initial operation, the sodium bicarbonate is added into mother liquor to prepare the stripping feed solution after recirculation, only the sodium bicarbonate is consumed, and the consumption of it is 1.36t NaHCO₃/t U.

4) The consumption of NaOH
The primary consumption of sodium hydroxide occurs in precipitation. Since the uranium concentration of stripping solution is high, the alkaline consumption is low, which is 0.95t NaOH/t U.

| Table 1. Consumption comparison of two processes |
|-----------------|-----------------|-----------------|-----------------|
| Reagent type    | Unit price (CNY/t) | Acid sodium chloride elution | Eluex process |
|                 |                  | Consumption (t (t·U)⁻¹) | Cost (CNY(t·U)⁻¹) | Consumption (t (t·U)⁻¹) | Cost (CNY(t·U)⁻¹) |
| $H_2SO_4$       | 700              | 1                      | 700              | 0.38              | 266               |
| NaCl            | 900              | 4.63                   | 4167             | —                 | —                 |
| NaOH            | 3000             | 1.33                   | 4000             | 0.95              | 2850              |
| TBP             | 25000            | —                      | —                | 0.0034            | 85                |
| P204            | 20000            | —                      | —                | 0.014             | 280               |
| kerosene        | 9000             | —                      | —                | 0.176             | 1584              |
| NaHCO₃          | 2000             | —                      | —                | 1.36              | 2720              |
| sum             | —                | 8867                   | —                | 7785              |                   |

Calculating by the current market price of reagent, the cost of these two processes is shown in table 1. From this table, it can be seen that the total cost per tone of uranium is 8867 CNY in ion exchange process, while 7785 CNY in Eluex process.

5. Conclusion
The two process flows of acidic NaCl elution and Eluex are employed to recovery uranium from low concentration leach liquor of acid in-situ leaching. Although there is no operation of extraction and stripping in the process of acidic NaCl elution, the Eluex process flow is more economical and environmental due to transportation operation of barren resin, large amount of Na₂SO₄, large quantity of effluent and high consumption of reagent in the process of acidic NaCl elution.

The further comparative work, includes investment of equipment, facility and construction as well as operation staff, should be considered in the future.

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