Study on carbonation technology of alkaline uranium mother liquor

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Abstract: The characteristics of the main components of alkaline uranium mother liquor: A small amount of uranium, a certain amount of hydroxide, and a large amount of carbonate. Through the analysis of chemical reaction and diffusion about transfer between mother liquor and CO$_2$, the influencing factors of mother liquor carbonation were determined: Gas-liquid transfer, reactant concentration, reaction temperature, etc. Tower counter-current was selected to investigate the influence of different types of fillers on carbonation effect. The stainless steel triangular spiral filler was optimized. The filling tower device for carbonation of uranium mother liquor was finalized, which greatly improved the gas-liquid distribution efficiency and carbon dioxide absorption rate. The effect of residual alkali concentration and reaction temperature of mother liquor on carbonation effect was investigated. The technology realizes the conversion of sodium hydroxide to sodium carbonate in the mother liquor. When sodium carbonate is converted to sodium bicarbonate, it can be converted to the saturated concentration of sodium bicarbonate, and CO$_2$ is absorbed in both stages. The device can be used to control the degree of carbonation of the mother liquor according to the demand, and be returned as leaching agent or eluent, realized the full reuse of the remaining alkali in the mother liquor.

1. Introduction
In China, there are many alkaline uranium resources. Considering the economic cost, most of these uranium ores are treated by alkali method, so a large number of alkaline solutions are produced. The mother liquor of uranium is one of them. At present, ion exchange process is basically used to extract uranium from alkaline solution, so the composition of mother liquor of uranium mainly depends on eluent. When the leaching agent is sodium carbonate + sodium bicarbonate, the main components of the mother liquor are uranium, sodium hydroxide and sodium carbonate$^{[1-3]}$. Uranium concentration is usually below 50mg/L, sodium hydroxide concentration is 5-20g/L, and sodium carbonate concentration is generally 60-100g/L$^{[4]}$. This part of mother liquor is difficult to be directly used due to its high pH; If neutralization is carried out, not only a large amount of reagents will be consumed, but also part of uranium metal will be lost, resulting in a waste of resources. Therefore, this study plans to use CO$_2$ to carbonate the mother liquor, convert it into carbonate and bicarbonate, and then return to use, so as to realize the recycling and reduction of waste.

2. Dynamic analysis of carbonation of uranium mother liquor
The mother liquor is liquid and CO$_2$ is gas. The reaction process between them includes both the diffusion between gas and liquid and the chemical reaction between CO$_2$ and the components in the
mother liquor. The chemical reaction process between component of the mother liquor and CO2 can be divided into three stages:

Stage one: NaOH→Na2CO3
The second stage: Na2CO3→NaHCO3
Stage 3: CO2(gas)→CO2(liquid)(a small amount of CO2 continues to dissolve until equilibrium)
The total reaction equation is: CO2(gas)+OH⁻→HCO3⁻

Firstly, the reaction rate between the mother liquor and CO2 was measured. The mother liquor consists of 5g/L NaOH+60g/L Na2CO3, and the determination results are shown in figure 1.

Figure 1. The reaction rate of the mother liquor at different temperatures

The experiment shows that the higher the temperature is, the faster the reaction rate will be. The main reason is that the higher the temperature is, the more energy will be obtained by the OH⁻ and CO3²⁻ in the CO2 and the mother liquor, and the higher the proportion of activated molecules will be. Macroscopically, the faster the reaction rate will be. Experiment also found that, as the reaction progresses, reduce reactive ion concentration in solution, the reaction rate is gradually reduced, the main reason is that the greater the concentration of reactants, the reaction particles collision probability increase, increases the chances of old bond rupture and new bond form, so as the reaction progresses, reaction particle concentration decreases, the reaction rate also gradually reduced. Therefore, the carbonation efficiency can be improved by increasing the temperature of the mother liquor and the concentration of reactants.

For the diffusion process, the rate can be calculated according to Fick's first law of diffusion: at a certain temperature, the ratio of the amount of substance B diffused through the cross-sectional area As to the product of the proportion of dN/dt to the cross-sectional area As and the concentration gradient dC/dx [5], i.e.

\[ \frac{dN_B}{dt} = -DA \frac{dC_B}{dx} \]

In the formula, D is the diffusion coefficient, unit is m²·s⁻¹.

For spherical particles, D can be calculated according to Einstein -- Stokes equation:

\[ D = \frac{RT}{6\pi r \eta} \]

In the formula, L is avogadro's constant;
\( \eta \) is the viscosity;
\( r \) is the radius of a spherical particle.

According to the formula, the higher the temperature is, the higher the diffusion rate is, and the smaller the carbon dioxide bubbles are, the higher the diffusion rate is. Because the diffusion process is the migration phenomenon generated by the thermal motion of particles, the higher the temperature is, the faster the particle moves, so it is more conducive to the diffusion of gas in the solution. Reducing the size of carbon dioxide bubbles can improve the contact area between gas and mother liquor, and increasing the number of bubbles and improve the degree of gas-liquid mixing. Therefore, when selecting the reaction device, it is necessary to select the device that can control the reaction temperature and improve the gas-liquid distribution effect.
So using carbon dioxide to carbonate mother liquor is technically feasible, and it can be implemented, the key is choose the appropriate devices, can satisfy the gas-liquid contact area and gas liquid concentration, heating requirements, guarantee the mass transfer speed, the chemical reaction speed, to improve the conversion efficiency and conversion rate.

3. Filler selection and process test of carbonation for mother liquor

The filler tower is a mass transfer equipment with the fillers in the tower as the contact components between gas and liquid. The tower is filled with suitable fillers to disperse the carbon dioxide gas and the mother liquid, and increase the contact area, accelerate the mass transfer rate and chemical reaction speed, and improve the carbonation efficiency. The filler tower can realize the mother liquor be added from the top of the tower, carbon dioxide gas be added from the bottom of the tower, they countercurrent contact in the tower, increase the concentration difference, improve the chemical reaction rate. Adding a layer of heating device to the outer wall of the filler tower can control the reaction temperature. According to the study of mother liquor and the investigation results, it is considered that it is more suitable to carry out the carbonation test of mother liquor in filler tower.

3.1 Selection of carbonation filler for mother liquor

Experiment design and manufacture the small filler tower, tower body is made of glass, specifications Ø 30 mm * 2500 mm, filler loading height 2000 mm, the outer wall of filler tower covered with heating device, temperature can be adjusted according to the test requirements, mother liquor fluid volume is about 50 mL·min⁻¹, CO₂ is about 400 mL·min⁻¹, The carbonation effects of 15mm * 15mm lasseau ring, 16mm * 16mm baler ring, 25mm * 12.5mm step ring, 25mm * 20mm saddle filler, 2.5mm * 2.5mm stainless steel triangular spiral filler and 3mm * 3mm Θ ring filler were compared in this study. The simulated mother liquid consisting of 10g/L sodium hydroxide and 80g/L sodium carbonate. The test results are shown in Table 1.

| Filler Type     | Specifications | Temperature of the tower/℃ | Amount of mother liquor feed/ (mL·min⁻¹) | Air inflow of CO₂/(mL·min⁻¹) | The mother liquor component after carbonation(g·L⁻¹) | The absorption rate of CO₂/% |
|----------------|----------------|------------------------------|-----------------------------------------|-----------------------------|----------------------------------------------------|----------------------------|
| lasseau ring    | 15mm×15mm      | 23.2                         | 50                                      | 400                         | 98.35                                              | 5.22                      |
| baler ring     | 16mm×16mm      | 23.4                         | 52                                      | 410                         | 87.16                                              | 16.14                     |
| step ring      | 25mm×12.5      | 23.1                         | 46                                      | 400                         | 89.25                                              | 13.41                     |
| saddle filler  | 25mm×20mm      | 23.9                         | 48                                      | 390                         | 80.47                                              | 17.36                     |
| triangular spiral | 2.5mm×2.5mm | 23.7                         | 49                                      | 420                         | 41.25                                              | 81.87                     |
| Θ ring         | 3mm×3mm        | 23.1                         | 54                                      | 410                         | 84.17                                              | 21.26                     |

The results show that, under the same conditions, except for the 2.5mm * 2.5mm stainless steel triangular spiral filler can absorb 100% CO₂, the CO₂ absorption efficiency of other types of fillers are less than 90%. The composition of mother liquor after carbonation was analyzed, and the degree of carbonation was basically the same as that of CO₂ absorption. The main reason is because of the 2.5 mm * 2.5 mm stainless steel triangular spiral filler structure characteristics, its each circle is a triangle, triangle stagger certain angle between circle and circle, and triangular spiral filler norms is lesser, gas can be fully break up after filler, and make mother liquor mixed with carbon dioxide gas, thus improving the reaction rate. Therefore, it is more appropriate to use 2.5mm * 2.5mm stainless steel triangular spiral filler.

3.2 Effect of mother liquor concentration and reaction temperature on carbonation

According to the preliminary basic research, the component concentration and reaction temperature of mother liquid have a great influence on carbonation, so the influence of the concentration and temperature of mother liquid on carbonation effect is investigated. The uranium precipitation temperature is about 50℃, combined with the actual industrial production, the temperature range selected as 15 to 40℃. See table 2 for test conditions and results:
Table 2. The effect of temperature on carbonation of mother liquor

| Setting temperature/°C | Tower temperature/°C | Amount of mother liquor feed/(mL⋅min⁻¹) | Precipitation mother liquor component/(g/L) | Air inflow of CO₂/(mL⋅min⁻¹) | The absorption rate of CO₂/% | Component after carbonation of mother liquor/(g/L) |
|------------------------|----------------------|-----------------------------------------|--------------------------------------------|-----------------------------|-----------------------------|-----------------------------------------------|
|                        |                      |                                         | NaOH                                       | Na₂CO₃                      | Na₂CO₃                      | NaHCO₃                          |
| 40                     | 40.6                 | 60                                      | 20                                         | 100                         | 250                         | 100                             | 126.97                         | 1.71                              |
| room temperature       | 39.8                 | 60                                      | 20                                         | 100                         | 1000                        | 100                             | 76.01                          | 78.21                             |
| 35.6                   | 5                   | 60                                      | 5                                          | 60                          | 60                          | 100                             | 65.22                          | 1.38                              |
| 35.6                   | 5                   | 60                                      | 5                                          | 60                          | 800                         | 100                             | 17.08                          | 77.29                             |
| 18.1                   | 60                   | 5                                       | 60                                         | 60                          | 800                         | 100                             | 14.94                          | 75.23                             |

By the test results, whether high concentration, and the simulated precipitation mother liquor of low concentration, at room temperature to 40°C can achieve the carbonation, Sodium hydroxide can switch to sodium carbonate completely, sodium carbonate can switch to the sodium bicarbonate saturation concentration. The mother liquor concentration decide the CO₂ input if CO₂ 100% reaction. The amount of intake CO₂ does not change much under different temperature, the reason is that the temperature is only changed the reaction rate, in the case of CO₂ by 100% reaction, the degree of reaction only associated with the volume of CO₂, so it can be seen that the test device within 15 to 40°C, 5-20 g/L sodium hydroxide concentration, and concentration of sodium carbonate in the 60-100 g/L range can achieve full use of CO₂.

3.3 Real mother liquor carbonation verification test

The carbonation test of uranium mother liquor was carried out. Composition of mother liquor: uranium concentration 0.040 g/L, sodium carbonate concentration 85.0 g/L, sodium hydroxide concentration 23.5 g/L, carbonation test results are shown in table 3.

Table 3. Carbonation test results of mother liquor containing uranium

| Setting temperature/°C | Tower temperature/°C | Amount of mother liquor feed/(mL⋅min⁻¹) | Air inflow of CO₂/(mL⋅min⁻¹) | Component after carbonation of mother liquor/(g⋅L⁻¹) | Remarks |
|------------------------|----------------------|-----------------------------------------|-----------------------------|---------------------------------------------------|---------|
|                        |                      |                                         |                             | NaCO₃                                             | NaHCO₃  | U                      |
| 40                     | 38.1                 | 60                                      | 300                         | 112.9                                             | 0.04    | 0.040                  | CO₂ gas has not escaped, it has been absorbed. |
| room temperature       | 39.8                 | 60                                      | 900                         | 68.8                                              | 77.2    | 0.040                  |
| 17.5                   | 60                   | 290                                      |                             | 113.8                                             | 0.32    | 0.041                  |
| 17.5                   | 60                   | 800                                      |                             | 70.1                                              | 72.2    | 0.039                  |

The test results show that the uranium precipitation mother liquid at room temperature to 40°C can achieve the carbonation successfully, sodium hydroxide can switch to sodium carbonate completely, sodium carbonate can switch to the sodium bicarbonate saturation concentration, uranium metal have no adverse effect on the process of carbonate. Before and after carbonation, the concentration of uranium metal in the mother liquor remained basically the same without loss. This equipment can be used for carbonation of real mother liquor.

4. Conclusion

(1) The test results show that the uranium precipitation mother liquid can achieve the carbonation successfully at room temperature to 40°C, sodium hydroxide can switch to sodium carbonate completely, sodium carbonate can switch to the sodium bicarbonate saturation concentration, uranium metal have no adverse effect on the process of carbonate, uranium metal without loss after reaction. It is shown that the method and equipment can be applied to carbonation for real mother liquor.
(2) The process of carbonation reaction is affected by reaction and diffusion. The reaction influencing factors are: reaction temperature and solution concentration. The diffusion influencing factors are: degree of gas-liquid mixing and temperature. The higher temperature, concentration and gas-liquid mixing degree, the faster the reaction rate is.

(3) This method can effectively reuse the mother liquor, reduce the effluent discharge, do not add other reagents, do not lose uranium metal, do not introduce other impurities in the whole reaction process. The mother liquor can return for utilization.

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