

# Study on Chemical Plug Removal Technology for Acid In-situ Leaching Uranium

**Li Po, Xu Ying, Liu Guo-Hong, Tan Ya-Hui, Cheng Wei, Hu Bo-Shi**  
Beijing Research Institute of Chemical Engineering and Metallurgy, CNNC  
145 jujukeshu, Tongzhou District, Beijing, China  
dijin@bricem.com.cn; yingxu323@163.com

**Abstract** - In-situ leaching mining technology refers to selective dissolution of metallic element containing in ore under the natural burial conditions through the chemical reaction of leaching agent and mineral. During the process of in-situ leaching of uranium by acid leaching, the chemical reaction between sulfuric acid and ore dissolving out iron, aluminum and uranium, and these metal ions are hydrolyzed and precipitated under the influence of pH. Meanwhile, under the long-term effect of sulphuric acid, the silicate ore formed silica gel hydrate of silicon dioxide and deposited in ore bed, which causes the chemical blockage. In this text, a method of chemical plug removal of ammonium bifluoride + sulfuric acid + citric acid is introduced for the improvement of permeability of ore bed and production capacity of drilling process, which is achieved by dissolving the siliceous compounds in ore bed by hydrofluoric acid.

**Keywords:** Acid In-Situ Leaching, Chemical Plugging, Ore Bearing Aquifer, Permeability.

## 1. Introduction

In-situ leaching of uranium means useful ingredients in liquid product are extracted by virtue of a circulatory system of liquid pumped and injected of drilling, thus, the amount of liquid pumped and injected of drilling remains as an important indicator of mine operation. In the course of in-situ acid leaching, sulfuric acid and ore produce chemical reaction, during which ions like Fe, Al and Ur spread into solution. Along with the migration of solution, the amount of sulfuric acid is down and pH value of solution is up. Chemical plugging is caused by the hydrolytic precipitation of metal ions and further causes the reduction of permeability of ore bed [1-2]. In the course of in-situ leaching and production, chemical plugging causes the larger amount of volume of injecting liquid over the volume of pumping liquid, which further leads to losses of uranium metal and leaching agent [3].

At present, repeated hole flushing is a general method to solve problems like this during in-situ leaching. However, conventional hole flushing is a temporary way for cleaning up mechanical obstruction around drilling, without effects to the chemical plugging in ore bed [4]. This study aims to offset the inadequacy of existing chemical hole flushing process and create a new technology for chemical plug removal of in-situ acid leaching, to completely settle problems of chemical plugging in ore bed, recover permeability of ore bed and increase the amount of liquid pumped and injected.

## 2. Geological background of mine and operation condition of mining area

The C2 acid mining area of a Xinjiang deposit is located between the No. 413-429 exploration line. The ore block is VII 1-8-1, VII 1-8-2 and VII 1-9-1, all of which are the seventh cycle uranium orebodies of the middle lower Jurassic Shui Xi Gou group (J<sub>1-2sh</sub>). The part of the thicker ore-bearing aquifer can reach 40 m. The ore body is mainly coarse sandstone, with 300 ~ 350m in the burial depth and 3.12m in the average thickness [5].

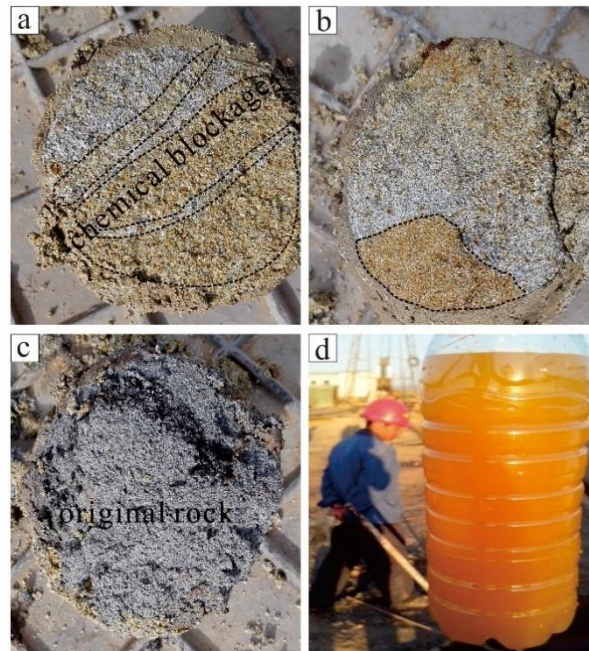
The drilling area of C2 mining area is "five-point type". In C2, there are 47 drilling holes, the distance between a pumping drill and an injecting drill is 28m and the thickness of ore body is 3.14m. When the drilling is checked, the water can reach more than 8m<sup>3</sup>/h. The productive hole has been put into acidification in November 2009. After seven years of operation, the water volume of a pumping drill is less than 2m<sup>3</sup>/h. The 542 t/tU of metal acid consumption per ton is several times more than that of similar mines. The pH of the leach solution collection has been maintained at 2.6, with no obvious residual acid being found [6].

### 3. Sample Collection and Chemical Analysis of Core Samples

In the C2 mining area, the whole core was taken for the ore section by an inspection hole was built for the chemical blocking serious pumping unit. Combined with the results of geological logging of core samples, geophysical logging and core dissolution, the core samples retrieved were classified and processed. Acid consumption test and simulated plugging test were carried out in laboratory.

#### 3.1. Analysis of Core Sample Appearance

A total of two layers of ore bodies are revealed by the inspection hole (Fig. 1): in the upper orebody, the presence that the gray sandstone is cemented by chemical precipitates, the cementation with yellow strip, causes serious chemical precipitation jamming; in the lower orebody, the constituent is gray sandstone. The extracted water in the ore layer is yellow and turbid, the yellow part of in which is obviously caused by  $\text{Fe}(\text{OH})_3$  precipitation.



a striped upper ore body; b. a bulk upper ore body;  
c. lower orebody; d. ore layer water  
Fig. 1: The core and ore layer water samples

#### 3.2. Chemical Analysis of Core Samples

Chemical analysis of sediment samples and core samples is carried out. The results are shown in table 1 and table 2.

Table 1: Chemical composition of water deposits in the ore layer.

chemical composition	$\text{SiO}_2$	$\text{Al}_2\text{O}_3$	$\text{Fe}_2\text{O}_3$	$\text{CaO}$	$\text{MgO}$	$\text{SO}_3$
content /%	12.64	8.38	40.15	8.02	1.04	24.38

The data of chemical analysis of sediment in the mine water indicate that most of the precipitated slag is Fe and Al hydroxide, silica hydrate and calcium sulfate.

Table 2: Chemical analysis results of core samples.

name of the sample	chemical analysis results /%						
	Fe	Ca	Mg	U	C	Al	S
YK-16-3	3.37	0.206	0.212	0.114	2.47	3.94	3.44
YK-16-4	12.2	0.152	0.246	0.165	0.89	3.76	10.42
YK-6g	1.95	0.236	0.477	0.05	2.47	6.25	0.012
YK-6y	5.25	0.248	0.554	0.01	0.82	5.81	0.39
YJ	2.43	1.47	0.924	0.01	2.39	9.57	0.154

Table 2 shows that the major acid-consuming minerals are iron and aluminum oxides, and the most lower core are YK-16-3 and YK-16-4. As shown in Figure 2, the lower core should not be eroded by acid, since the higher content of Fe and S indicates the core is mainly in the form of  $Fe_2S_3$ , and since the sample YK-6y is the core of the Yellow deposit cementation with the higher content of Fe and no high content of S indicating that  $Fe(OH)_3$  is the main existence in the lower core.

#### 4. Chemical Plug Removal Test

Based on the analysis of chemical blockage in acid mining area, the main components are  $Fe(OH)_3$ ,  $Al(OH)_3$ ,  $CaSO_4$  and amorphous silica colloid ( $xH_2O \cdot ySiO_2$ ).

##### 4.1. Simulated Plug Removal Test

Selecting blockage relieving agents such as citric acid (NMS), hydrochloric acid, acetic acid (YS),  $NH_4HF + H_2SO_4$ , doing simulated plug removal test explores preliminarily the complexation of organic ligand with iron. The results of the test are shown in Table 3.

Table 3: Simulation results of plugging test.

plugging agent	NaOH /mL	after precipitation		after clarification of plugging agent		Iron dissolution rate /%
		pH	$Fe^{3+}/(g/L)$	clarification solution pH	$Fe^{3+}/(g/L)$	
1g/L HCl	9.2	4.10	0.01	2.33	0.53	21.85
2g/L HCl	9.0	4.11	0.01	2.13	1.14	47.75
3g/L HCl	8.0	4.13	0	1.84	1.615	72.11
5g/L NMS	9.2	4.60	0	2.45	1.52	67.87
10g/L NMS	8.6	3.93	0	1.95	2.15	96.04
15g/L NMS	8.0	3.94	0	1.77	2.834	100
20g/L NMS	8.8	4.01	0.01	1.64	2.92	100
5g/L YS	8.8	4.01	0.01	3.01	0.051	1.74
10g/L YS	8.8	3.95	0.01	2.93	0.21	8.48
15g/L YS	8.0	3.99	0	2.86	0.617	27.55
20g/L YS	8.0	3.96	0	2.83	0.617	27.55
$NH_4HF + H_2SO_4$	8.7	3.95	0.12	2.03	1.96	90.3

It can be seen that citric acid has better dissolution effect on  $Fe(OH)_3$ . When the concentration of citric acid is 10g/L, the dissolution rate of iron can reach 96.04%. In addition, ammonium fluoride and sulfuric acid can dissolve  $xH_2O \cdot ySiO_2$  in the blockage [7] and achieve the effect of HF. Ammonium fluoride and citric acid are ultimately selected as the blockage

relieving agents with faster rate and higher efficiency of dissolution. The two agents can dissolve iron aluminum oxide and silica colloid.

#### 4.2. Core Sample Plug Removal Test

The core samples were weighed 50g in the triangle bottle, then adding respectively 5% acetic acid, 10g/L citric acid, 20g/L citric acid and 5g/L  $\text{NH}_4\text{HF}+2\text{g/LH}_2\text{SO}_4$ . The ratio of liquid to solid was 5:1, and the stirring leaching span is 48h. The solution obtained by filtration after the end of the leaching was analyzed to get the dissolution results with iron and aluminum shown in Table 4.

Table 4: Analysis result of core sample plugging test.

plugging agent	analysis result of dissolution solution /(g/L)				iron dissolution rate /%	aluminum dissolution rate /%
	$\Sigma\text{Fe}$	Al	$\text{SiO}_2$	pH		
5% YS	0.302	0.0567	0.02	2.68	5.99	0.30
10g/L NMS	1.24	0.372	0.06	2.43	25.5	1.94
20g/L NMS	1.55	0.528	0.15	2.15	31.9	2.76
5g/L $\text{NH}_4\text{HF}+2\text{g/LH}_2\text{SO}_4$	2.36	1.94	0.87	1.95	48.6	10.1

The test results show that the citric acid system has iron dissolution rate of 31.9%, and has little effect on  $\text{SiO}_2$  colloid, since organic acid is weak acid.  $\text{NH}_4\text{HF}$  and  $\text{H}_2\text{SO}_4$  play the role of HF, that is, it can dissolve iron and aluminum hydroxide precipitates on the surface, and also  $\text{SiO}_2$  colloid and the iron and aluminum minerals in the sample. Calculating the dissolution rate is based on the amount of iron and aluminum contained in samples, thus it has a large difference with simulated plug removal test.

#### 4.3. Field Chemical Plug Removal Test

##### (1) Field chemical plug removal method

Combined with the location of the inspection hole, the chemical analysis of core samples indicates that the chemical blockage has been formed in the range of at least 10m extending from the center of the pumping hole to the surrounding area. In order to dissolve and migrate the plug to the surface, and finally relieve blockage, the blockage relieving agents need to contact with the blockage at first. The concrete plug removal method are as follows:

##### Static chemical well-flushing method:

During the conventional washing used by an air compressor, monitoring the amount of water out of the drilling hole, taking the samples of the final liquid, and analyzing the content of target elements, were carried out. A certain concentration of  $\text{NH}_4\text{HF}$  and  $\text{H}_2\text{SO}_4$  solution was added to the drilling hole. After the hole was sealed for 48 hours, the washing liquid was extracted with the air compressor. The content of target elements in washing liquid was analyzed. It is the static chemical washing stage.

##### Pressure diffusion well-flushing method:

A certain concentration of  $\text{NH}_4\text{HF}$  and  $\text{H}_2\text{SO}_4$  solution and citric acid solution were added into the drilling hole. The hole was pressurized the leaching agent by connecting the injection system. The injection pressure is 0.6 to 0.8MPa, and the duration is 72 hours. The migration radius of the blockage removal agent can be expanded as far as possible to fully dissolve the blockage and relieve blockage and increase permeability.

##### (2) Analysis of the effect of plug removal

Table 5 is the results of chemical analysis of related elements in the extracting samples from static chemical washing. The last behavior is the average value on extraction of 2# mining area. It can be seen that the content of Fe,  $\text{Fe}^{3+}$  and  $\text{Al}^{3+}$  increases obviously, which is the result of the reaction of the blockage relieving agents and the blockage as  $\text{Fe}(\text{OH})_3$  and  $\text{Al}(\text{OH})_3$ ;  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$  have no obvious changes, indicating that the blockage relieving agents do not play a role on  $\text{CaSO}_4$ .

Fig.2 is the statistical data of pumping and injection amount before and after plug removal (production and operation data, pressure 1.2MPa before plug removal, and injection pressure after plug removal is only 0.7MPa). The results show that after the chemical plug removal, the injection amount of Z-0217 and Z-0218 is increased by 30% and 45%, respectively, and the pumping amount of the C-0211 is increased by more than 40%. Continuous tracking and statistics of production and operation data for about 60 days showed that the amount of pumping and injection remained at the same level, and there was no obvious downward trend. It indicates that the plugging agent reaches the deep part of the ore layer, and the chemical plugging is dissolved, which improves the permeability of the ore layer and dredge the leaching channel.

Table 5: Analysis results of static chemical well-flushing related elements.

well number	U/ (mg/L)	Fe/ (mg/L)	Fe <sup>3+</sup> / (mg/L)	Al <sup>3+</sup> / (mg/L)	Ca <sup>2+</sup> / (mg/L)	SO <sub>4</sub> <sup>2-</sup> / (g/L)	H <sup>+</sup> / (g/L)
0211	1.53	661	397	342	560	6.8	2.52
0217	2.07	826	374	368	465	9.76	3.52
0218	2.93	826	363	357	483	9.59	5.25
C2	12.1	480	8.0	78.8	560	10.2	

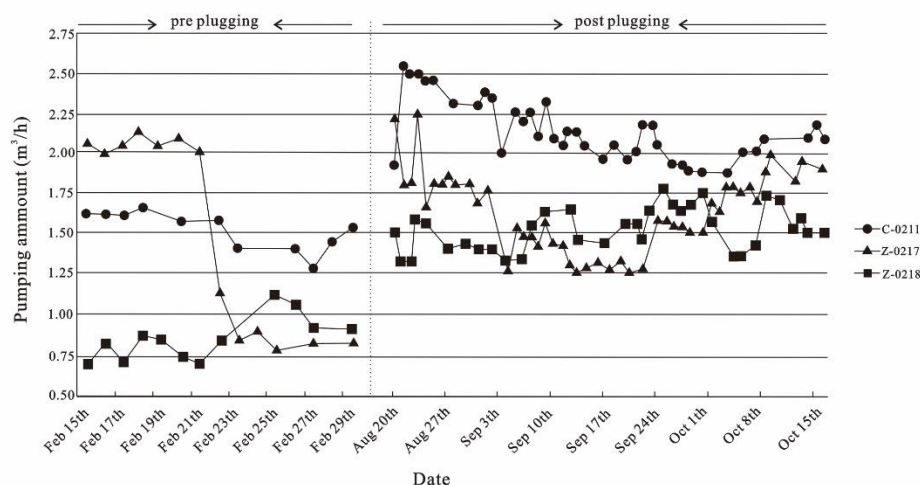


Fig. 2: The amount of pumping and injection before and after chemical plugging.

## 5. Conclusion

A method of chemical plug removal for in-situ leaching uranium has been formed through research. The core technology is ammonium hydrogen fluoride + sulfuric acid + citric acid complex plug removal process. The main principle of hydrogen fluoride ammonium plugging is that hydrofluoric acid can be generated by ammonium hydrogen fluoride and sulfuric acid under the condition of high concentration of sulfuric acid. Hydrofluoric acid dissolved silica colloid in the ore bed, restored the permeability of the mineral layer around the drilling filter, and increased the amount of pumping and injection. The application result of mine plug removal shows that this technology can increase the amount of pumping and injection by more than 30%. The technology can be used for similar mines in China.

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