PROCESSING PA LUA URANIUM ORE BY MIXING AND CURING WITH SULFURIC ACID ON A SCALE OF 500 KG/BATCH TO RECOVER YELLOWCAKE

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ABSTRACT: Uranium ore in Pa Lua area is sandstone with different levels of weathering. This kind of ore contains calcium and clay that may cause clogs during heap leaching. In this study, a technique of mixing and curing with strong acids is used and followed by washing to recover uranium. This study also focuses on study of ore processing issues such as crushing, regenerating particles in fine ores, mixing, curing and washing. The leach solution is treated by ion-exchange and precipitation of products by NH_4OH. The experiment results show that regenerating a portion of fine ores, mixing and curing help washing residues in the column more effectively. Flow rate of the input solution can be controllable and stable. Columns don't clog even when washing takes place in the ore column of 5 meters high. Efficiency of uranium recovery can reach to 85-90%. Products of technical uranium are obtained with high quality.

Key words: Uranium, uranium ore processing.

Introduction

Facing the risks of depletion of uranium sources and sharply rising price of uranium, besides, looking for solutions of renovating fuel cycle and producing new generation of reactors, many companies have strengthened exploration of new uranium ores and paid more attention to low-grade ores. Moreover, from the beginning of 2006, the Government has officially allowed to build the first nuclear power plant in Vietnam in order to put it into operation around the period of 2017 - 2020. In this context, continuing research for completion and selection of the most appropriate technology for uranium ore processing in Vietnam is extremely necessary and crucial. This is in line with the development trend in the world and at the same time helps gradually produce locally fuel for nuclear power plants.

The project entitled " *Processing Pa Lua Uranium by Technique of Mixing and Curing at a Scale of 500 kg/batch to Recover Technical Uranium*" was set up to conduct additional researches on several technical issues of mixing and curing with acid and washing to recover uranium from sandstone ores in Pa Lua area to complete a set of data in ore processing procedure, to develop an appropriate technological procedure for ore processing, calculating and designing several main equipments based on the data obtained from the study and previous ones.

Basics of the method

In water, sulfuric acid is dissociated into sulfate, bisulfate and hydrogen ions. These ions react with uranium (VI) in ores to create sulfate uranyl and complexes of sulfate uranyl. Depending on concentrations of acid and uranium, temperature and other complexes in the system, there may be any type of uranium in the solution. Uranium in the ore under the form of U (IV) must be oxidized before the dissolution takes place. It is Fe^{3+} ion that is oxidant in the oxidation reaction of U (IV) in leaching precess by sulfuric acid. Iron is always present because the ore contains iron. In addition, during crushing and grinding ores, iron is also added due to abrasion of the equipment. However, to maintain Fe^{3+}, a certain amount of oxidants is needed.

Acid consumption is a function of constituents in the ores. Calcite, dolomite, magnetite and siderite react with acid right at the zone of low acid concentration and normal temperature. Sulfide, metal iron, several types of phosphate, molybdate, vanadate, oxides, flouride etc. consume acid and contaminate solutions when temperature or acid concentration increases.

In the process of mixing and curing with acid, most reaction of acid with minerals complete. Washing solution through the next layer is just simply to rinse residues to recover uranium. In the void of ore layer, there is air together with solution; therefore, leaching is an unsaturated system. Thus, to control leaching, it is necessary to pay attention to the conditions of complicated flow for hydraulics of unsaturated area. Two key issues of hydraulics are sufficient flow and (or) uniform flow through the ore heap. Sufficient flow is necessary so that the ore heap is percolated in an appropriate duration (cost effective) while uniform flow is necessary to allow the whole ore body is well leached. Leaching and washing require the ore body to have relatively well infiltration and the materials need to be uniform to avoid channels in the flow. Any portion of the ore body if not contacted well to the solution, will not be leached or rinsed.

Concerned ores

Sandstone ores used in the research have different weathering degrees. Sizes of non-weathered and semi-weathered ores are pretty large, mostly over 20 cm. Weathered ore is under the powder forms.

Main minerals of this sandstone ore are quartz (SiO_2), albite ($NaAlSi_3O_8$), glauconite ($(K,Na)(Fe^{+3},Al,Mg)_2(Si,Al)_4O_{10}(OH)_2$), calcite ($CaCO_3$), kaolinite ($Al_2Si_2O_5(OH)_4$), sericite ($K_2O.3Al_2O_3.6SiO_2.2H_2O$), illite ($(KH_3O)Al_2Si_3AlO_{10}(OH)_2$), siderite ($FeCO_3$), sphene ($CaO.SiO_2.TiO_2$). Mineral containing uranium is mainly Nasturan ($(U,Th)O_2.(O_{0,5-3})UO_3.xPbO$).

Uranium content in the ore is about 0.053–0.058%. The most abundant impurities are silica (average 75%), aluminum (>5%), iron (1%), potassium, sodium and alkaline metals (calcium in the non-weathered ores even reaches >0.9%) and many other impurities. Distribution of uranium based on particle sizes is relatively uniform.

Non-weathered and semi-weathered ores need to be crushed into particle sizes appropriate for chemical treatment.

Results and discussion

1. Crushing ores and calculating energy for crushing

For crude pieces of ores (>10 cm), it is needed to crush according to two levels (using crusher). In the first level, size is decreased to <10 cm, then in the second level, the size is decreased to appropriate size for mixing and curing stage.

When comparing grinding features of non-weathered and semi-weathered ores, it is shown that porosity of non-weathered ore is larger than that of semi-weathered one. In addition, non-weathered ores have less hardness. Most ore particles after crushing have their size bigger than 0.6 mm. Portion of fine particles that can cause clog in the ore column accounts for relatively low, less than 10%. Therefore this portion needs to be aggregated into bigger size depends on their impacts to the further treatment stages. The smaller width of the voids is, the higher fine portion is. It is possible to reduce the amount of fine ore by selecting an appropriate crushing condition that is without adjustment of the width of crushing gap to a certain value and with circulation of crude ore portion. However, it is also needed to pay attention to energy consumption and any raised issue.

For non-weathered and semi-weathered ores, to produce ore particles appropriate to heap leaching, using jaw crushing is the most appropriate. In order to get the ore with appropriate size for mixing and washing, appropriate width of the gaps between crushing bars in the second level is 20 mm.

In terms of energy, BOND formula has been used. For sandstone ore with average hardness, energy consumption for crushing 1 tone of ore with sizes reduced from 20 cm to 2cm is 0.46kW. However, in reality, depending on productivity of the equipment and operation, the real energy consumption may increase in comparison to the above calculated values. Results of calculation of consumed crushing energy will be used as basis for calculating capacity and productivity of crusher.

2. Recreating fine ores

The purpose of this process is to make ore portion of fine particles become particles with size large enough to ensure that washing process is not disturbed due to clogging or blocking the flow of solution. In addition, particles need to remain stable in leaching medium of acid. Uranium leaching efficiency needs to be at an acceptable degree without considerable impacts to the total efficiency of uranium recovery from the ores.

When investigating factors impacting to the process of recreation of particles, it is shown that necessary moisture content is 15 - 16% and duration of 14 - 16 minutes are needed. For the ore with size of -300 μm, the amount of liquid glass as adhesive appropriate for each type of non-weathered, semi-weathered and weathered ores are 6.9%; 6% and 4%, respectively. To strengthen ability of solidifying of the obtained pellets, Na_2SiF_6 is added with the rate of 1%. These agents mixture is selected for research because it creates pellets with certain stability after mixing and curing with strong acid while other agents do not have these characteristics. Results of trial of immersing in acid, ore pellets obtained in appropriate condition are as follows.

Table 1: Efficiency of uranium leaching and degree of particle broken down when creating particle in appropriate conditions

Ores	Efficiency of U recovery (%)	Degree of particle broken down (%)
Non-weathered	78.32	12.6
Semi-weathered	66.67	2.8
Weathered	63.86	13.7

Thus, after pelletizing, efficiency of uranium recovery partly reduces while acid consumption considerably increases (e.g. ordinary non-weathered ore when mixed and cured just consumes 50 kg acid/ ton of ore, but after pelletizing, this figure increases to 95 kg/ton of ore to reach uranium recovery over 75%. For semi-weathered ores: 35 kg/ton of ore, 80 kg/ton of ore and 66%, respectively). Degree of complete breaking down of pellets is in the acceptable range. The bigger initial ore particle size is, the more cost of agents is and the more difficult palletizing is.

Based on the above research results, in case it is necessary to pelletize, only portion of ore with particle sizes less than 0.3 mm needs to be pelletized. In that case, it is acceptable that acid consumption increase not much while efficiency of uranium recovery decreases a bit. If the ore contains a large portion of fine particles, the use of this method needs to be reconsidered because the efficiency of uranium recovery is impacted considerably. Moreover, high acid consumption and high operational cost can cause the increase of production price.

3. Mixing and curing

Several parameters related to ore mixing, curing and washing processes such as capability of water retention, void volume of the heap etc. are paid attention. In the ore body, water can be in the capillaries of ore particles, in the gap among ore particles and stick on the surface of particles and the wall of columns. For each ore particle size, the following parameters are determined (table 2). According to the results, the larger ore particles, the less water retention; therefore, it is very difficult to carry out mixing and curing process.

Table2: Capability of remaining water and void volume of all types of ores according to sizes of ore particles

Particle size (mm)	Moisture content (%)		Total void volume (%)	
	CPH	*BPH*	*CPH*	*BPH*
+ 20	1.4	2.0	59.2	58.5
- 20 + 10	3.7	6.0	57.5	57.8
-10 + 5	6.9	8.6	58.8	57.6
- 5	19.0	20.0	46.0	44.7

However, if ore body consists of many degrees of particle size with a certain ratio, due to the mixing of different ore sizes, degree of water retention and bulk density change (table 3), creating a favorable condition for reaction.

Table3: Distribution of particle size

TT	Particle size (mm)	Weight ratio (%)		
		Non-weathered	*Semi-weathered*	*Weathered*
1	+20		7.72	
2	+10 - 20	11.72	39.27	
3	+5 - 10	46.32	12.72	12.0

4	+2.36 - 5	13.62	5.83	5.6
5	+1.18 - 2.36	7.41	8.03	13.6
6	+0.6 - 1.18	6.91	8.24	30.4
7	+0.3 - 0.6	7.09	10.30	23.8
8	-0.3	6.93	7.90	14.6

Table 4: Degree of water retention and void volume of ores with many degrees of particle sizes

Ore type	Moisture content (%)	Total void volume (%)	Bulk density
Non-weathered	10.3	49.6	1.51
Semi-weathered	12.1	50.6	1.33
Weathered	20.2		

Determining water retention of ores allows us to calculate necessary amount of water during mixing and curing with strong acids.

During mixing and curing process, only a small part of acid is used to dissolve minerals containing uranium while most part of the acid is consumed by other minerals in the ore, especially carbonate (as in the case of non-weathered ore). Specific acid consumptions for each type of ores are as follows: non-weathered - 50 kg/ton, semi-weathered - 35 kg/ton and weathered ore - 30 kg/ton. If ore contains different minerals, acid consumption will be higher than the average value calculated according to the certain ratio. For example, acid consumption of 46 kg/ton is needed for the ore containing non-weathered and semi-weathered parts with a ratio of 1/1.

After mixing and curing with strong acid, initial ore particles are broken down into smaller sizes, especially for non-weathered ore. Degree of breaking down depends on initial particle size, acid concentration, duration of curing and degree of weathering. Therefore, degree of water retention as well as other parameters of ore residues changes a lot. Now, different levels of particle size stick together leading to the increase of water retention and the decrease void volume (see table 5).

Table5: Some features of ore tailings

Type of tailings	Moisture content (%)	Total void volume (%)	Bulk density
Non-weathered	16.2	37.9	1.55
Semi-weathered	14.3	39.0	1.47

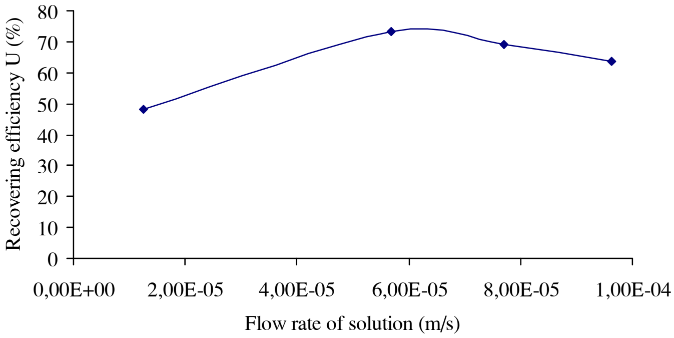
However, the ratio of fine particles (<0.3 mm) almost does not increase. Obviously, when reacting with strong acid during mixing and curing, some products from reaction under the form of precipitant such as calcium sulfate, SiO_2, etc. aggregate fine particles together or with larger particles. This is an advantage for washing uranium in the next stage.

When investigating affect of oxidants to the efficiency of uranium dissolution, it is found that in non-weathered and semi-weathered ores, a part of uranium existing under the form of U (IV) cannot dissolve in acid solution. Therefore, an amount of oxidant to maintain iron concentration (Fe III) to supply for oxidizing reaction of U (IV) is required (around 3 kg/ton).

After being mixed with acid, the mixture is cured for 3 days. It is important that only after curing process is completed, the whole ore body is moved to columns or heaps to rinse for uranium recovery. If the ore is placed into the column right after completion of curing, the ore body will be pressed; therefore, fine particles will cause clog during washing process.

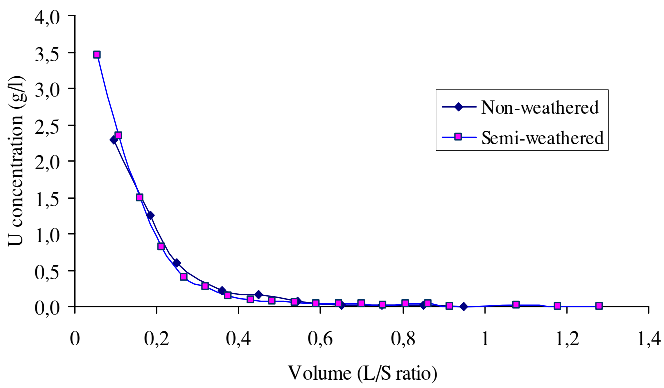
4. Washing for uranium recovery

After trials of options for washing ores that are mixed and cured with acid, it is found that the technique using batch washing should be used in combination with leaching. Based on this technique, at several initial washing times, the solution has pH value of 1. When each washing time is completed, the solution appears at the bottom of the column. When the solution mostly doesn't flow, it is the time to continue washing. Solutions with higher pH or clean water are used for washing residues. In the first washing times, total amount of solution released from the column will be smaller than the total amount of solution provided to the column because a part of solution is remained to maintain moisture content (the moisture content of residues increases) and time for the solution to break through the column will be longer than that of the further times of washing. This technique allows saving retention time of solution in the ore body so that reaction continues and amount of water needed is reduced. Efficiency of uranium recovery increases. For example, for non-weathered ore and semi-weathered ore, efficiency of uranium recovery can be 78% and 84.3% respectively while if solution with pH 2 is continuously rinsed, efficiencies can be 73.1% and 81.6%, respectively. The rate of washing is controllable.



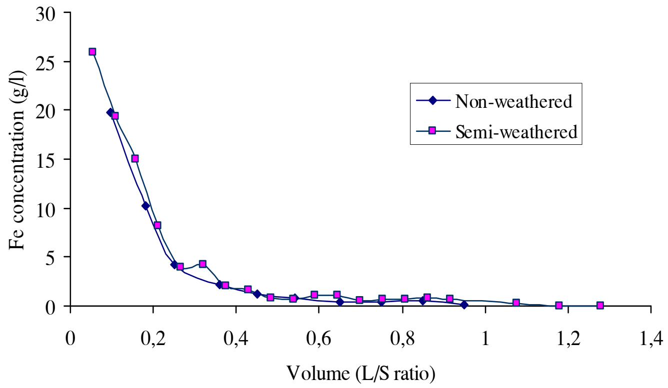
Ficgure 1. Effect of washing flow rate on uraium recovering efficiency (non-weathered ore)

Although after mixing and curing, all levels of particle sizes are more distributed than that of direct leaching on the column, it is unavoidable that there is a phenomenon in which



Ficgure 2. Washing curve for uranium recovery

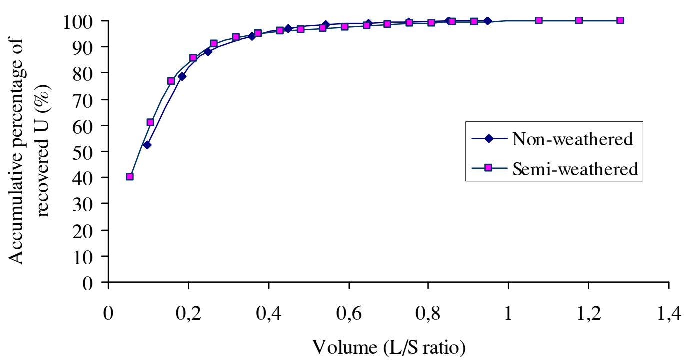
residues of crude ore stick together in one place and fine particles stick together in another place causing inconsistence. In the primary study, if the flow rate of washing is getting higher, solution is getting more priority to go through ore body with large size and vice versa. Only when the flow rate is in a certain range, flow of solution will be likely consistent in the ore body. Therefore, the flow rate of washing is the most affecting factor in washing process. When trying with non-weathered ore which is mixed and cured as well as continuous rinsed with the total volume of solution reaches a ratio of L/R = 1/1v (L/R = liquid/solid). Diagram in the Figure 1 shows that only in a certain appropriate flow rates (around 6.00E-05 m/s); efficiency of uranium recovery reaches the highest value at 73.1%.



Ficgure 3. Iron washing curve

Flow rate depends on particle size. The finer ore particles size is, the lower flow rate is. For instance, for mixed ores consisting of 3 types of non-weathered, semi-weathered and weathered ores with a ratio of 1/1/1 in the first washing time, flow rate from outlet of the column just reaches 1.9E-05 m/s, and then increases more and more in the next washing times. For such fine ores like the above ones, flow rate also depends on the height of ore layer. The higher height, the more pressed the ore. Because void space is very small, the flow of solution is also blocked. Therefore, flow rate also is much decreased (for the height of 5 meters, the flow rate of the first washing time only reaches 7.78E-06 m/s). Time for washing also increases considerably when the height of ore layer increases.

During washing process, uranium and dissolved substances are rinsed right in the first time (see Figure 2. 3 and 4). Results show that the change of concentration and amount of dissolved substances almost takes place with a total volume of solution at the L/R ratio of 1/3. After that, though more amount of solution is needed, the amount of dissolved uranium obtained is only some percentages. Therefore, to decrease solution consumption and increase uranium concentration, the part of dilute solution needs to be circulated in the next columns. The part of high concentration is moved to the next treatment stage as ion exchange and consequently, precipitation to get technical uranium products.



Ficgure 4. Accumulative percentage of recovered uranium with solution volume

Trial of processing ore on a scale of 500 kg/batch with mixture of non-weathered, semi-weathered and weathered ores at the ratio of 1/1/1 (height of ore layers in the washing column is up to 500 kg/batch) took place in a completely favorable condition. Washing is carried out with two stages, 6 times of washing without clogs of the column. Consumption of water when washing is just 1/3 of the weight of treated ores. Efficiency of uranium recovery reaches 85-90 %. Obtained solution contains around 1.2 g U/L.

After processing, the result obtained by using Amberlte IRA-420 resin in static column system, then followed by precipitation by agents H_2O_2 and NH_4OH, technical uranium with high quality (80% U_3O_8 and low contents of other metal impurities).

Conclusions

1. Using option of crushing at 2 levels in which the width of crushing gap at the second level of 20 mm is appropriate, can reduce the amount of fine ores. Energy consumption for this stage is 0.46 KW/ton of ore.

2. Regenerating particles in the portion of fine sizes which creates relatively stable particles in acid medium will have an ability to avoid clogging in the column when washing. However, this will cause the increase of acid consumption and partly decrease efficiency of uranium recovery, especially for semi-weathered and weathered ores. The larger initial size of ore particles, the higher degree of this change. This stage should only be applied for weathered ores with fine particles less than 0.3 mm on a scale in which the column is high.

3. During mixing and curing, ore is broken down too much, especially non-weathered ore. However, the portion of fine residues (less than 0.3 mm) mostly doesn't increase considerable, not causing any difficulty for the further process like washing to recover uranium. An appropriate mechanism for the stage is acid consumption of 30-55 kg/ton of ore; moisture content of 10-13%, oxidant 2-3 kg/ton of ore and curing duration of 3 days. After curing for 3 days, the ore needs to be cured before being placed in the washing column.

4. In the stage of washing, it is recommended that batch washing be applied and several initial washing times be used with pH 1 so that efficiency of uranium recovery can increase and the amount of washing water can be reduced. After mixing and curing process, flow rate of washing solution in washing stage can be controllable and stable in the whole process, avoiding column from being clogged. Appropriate flow rate of washing is around 6.0E-0.5 m/s. However, for weathered ores, the flow rate decreases considerably. Circulation of washing solution (2 stages) leads to the increase of concentration of uranium in the solution and reduction of water used.

When trying processing ores by mixing and curing, then washing on a scale of 500 kg/batch of ores, a solution containing 1.2gU/l was obtained. Amount of water consumed is equal to 1/3 ore weight. Duration for ore processing needs only 12 days. Efficiency of uranium recovery can reach up to 85-90%. Treatment of leaching solution by ion-exchange with amberlite IRA-420 resin is conducted and followed by precipitation to obtain product with concentration higher than 80% U_3O_8.

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