

DYNAMIC LEACHING OF URANIUM ORE FROM CAETITÉ'S FACILITIES – BA, BRAZIL – A COMPARISON WITH THE HEAP LEACHING PROCESS

Luiz A. Gomiero¹, Walter Scassiotti Filho¹ and Carlos A. Morais²

(1) Indústrias Nucleares do Brasil S/A – INB - Unidade de Caetité - BA
Fazenda Cachoeira s/nº - Zona Rural – Distrito de Maniaçu
Cx. Postal 7 – 46400-000 – Caetité – BA - Brazil
gomiero@inb.gov.br - scassiotti@inb.gov.br

(2) Centro de Desenvolvimento de Tecnologia Nuclear – CDTN/CNEN
Campus da UFMG - Pampulha - 30123-970 - Belo Horizonte - MG - Brasil
cmorais@cdtn.br

ABSTRACT

The production of uranium concentrate in Brazil is attributed to “Indústrias Nucleares do Brasil S/A – INB”, a federal government company. At the present the only uranium mining and milling facility, the “Uranium Concentrate Plant – UCP”, is located in Caetite, Bahia - Brazil, which works on uranium ore averaging 2.90 $\mu\text{g/g}$ U_3O_8 . The milling process starts with ore crushing, followed by heap leaching with a sulfuric acid solution, uranium separation, purification, and concentration through solvent extraction and chemical precipitation techniques. As the open-pit mine became deeper, the uranium recovery in the leaching process began to decrease due to the increasing presence of primary uranium minerals inside rock grains. The uranium content in the leached ore became too concentrated, reaching values higher than 700 $\mu\text{g/g}$ U_3O_8 . This paper presents a study of dynamic leaching of the ground ore with sulfuric acid. The following process variables were investigated: ore grain size, leaching time, oxidant type, sulfuric acid/ore ratio, and solids percentage in the ore pulp. The dynamic leaching results have shown that, depending on the grain size, the uranium content in the leached ore can be as low as 100 $\mu\text{g/g}$ U_3O_8 . Experiments of continuous dynamic leaching carried out with ore particle top size of 590 μ indicated a uranium recovery of 94%, approximately 20% higher than the recovery obtained in the heap leaching process. In this case the uranium content in the leached ore was 200 $\mu\text{g/g}$ U_3O_8 .

KEY-WORDS: uranium extraction, dynamic leaching, heap leaching.

1. INTRODUCTION

Brazil's internal uranium demand for power generation is approximately 400 metric tons in the form of U_3O_8 (Matos and Rubini, 1999). To meet this demand the federal government, through its state company, Indústrias Nucleares do Brasil S/A – INB, set up the uranium concentrate mining and milling facility, named Uranium Concentrate Plant – UCP, in Caetité county, which is located in the mid southern region of the State of Bahia. From an economic standpoint, uranium is the sole local mineral wealth, occurring mainly as a primary mineral uraninite in the main ore body. The uranite is covered by a layer of weathered ore containing secondary uranium minerals, that are easily solubilized by sulfuric acid solutions.

UCP is a mining and milling facility comprising an open-pit mine and a physical and chemical processing plant. The basic projected processing capacity is 180,000 ton/year of run-of-mine ore with an estimated average uranium content of 2.90 $\mu\text{g/g}$ U_3O_8 and an average uranium recovery of 70% to produce some 400 ton/year U_3O_8 as Ammonium Diuranate – ADU (Gomiero, 2006). The crushing and leaching flow sheet process is shown in Figure 1. The heap leaching technique of crushed ore was chosen after an economic feasibility study was undertaken at the end of the last century. At that time, there was not much funding available for the project as the uranium price in the foreign trade was as low as US\$ 10/lb U_3O_8 .

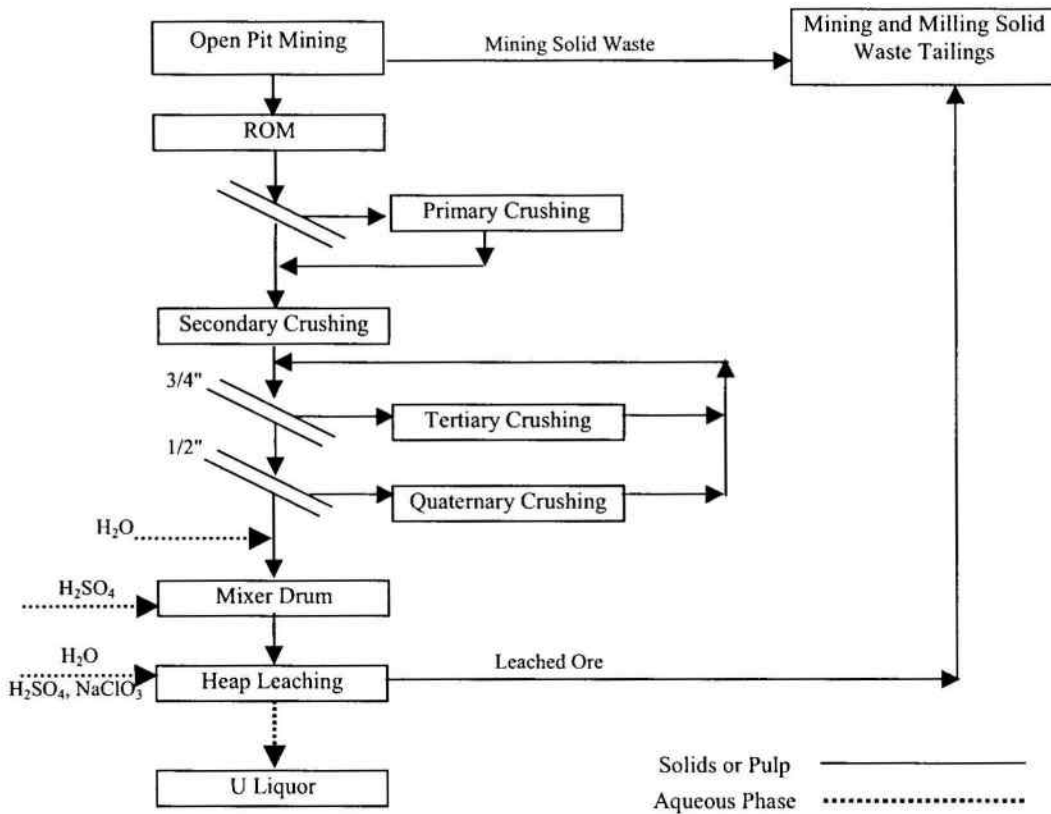


Figure 1 – Flow Sheet of the Crushing and Leaching Steps

From the plant startup in December 1999 to February 2007 approximately 1,435 tons as U_3O_8 have been produced at the milling facilities from the processing of approximately 800,000 tons of ore with an average recovery of 75 wt%.

As the open-pit mining became deeper the uranium recovery in the leaching step began decreasing due to the presence of primary uranium minerals inside the ore grains, which makes the uranium less available to the leaching solution. As a consequence, uranium content in the leached ore has risen to values as high as 700 $\mu\text{g/g}$ U_3O_8 . At the same time the uranium price in the foreign trade has continuously risen reaching approximately US\$ 85/lb U_3O_8 as of February 2007.

Currently there is a technical need for developing a new leaching process whose implementation would be economically supported by the current foreign trade uranium price. The technical alternative chosen to be studied is the dynamic leaching of the ground ore pulp in agitated tanks. Such mill leaching and solid/liquid separation equipments are available and ready to be used at the first Brazilian uranium mining and milling facility, which is presently being decommissioned, located in Caldas, MG – Brazil. These equipments can be conveyed to the UCP's facilities with great economic advantage.

This study was carried out at the Mineral Technology Laboratory of the "Centro de Desenvolvimento da Tecnologia Nuclear – CDTN", owned by the Brazilian "Comissão Nacional de Energia Nuclear – CNEN" located in Belo Horizonte, MG - Brazil

2. EXPERIMENTAL PROCEDURES

Chemical characterization of samples was based on qualitative analysis by X-ray fluorescence and quantitative analysis by ICP-AES, atomic absorption spectrophotometry, ion specific electrode potentiometry, UV-VIS spectrophotometry, flame photometry, and gravimetry. The process development was accompanied by energy-dispersive X-ray spectrometry (Kevex system) (Morais and Ciminelli, 2002). Replications prepared from randomly chosen experiments indicated an experimental error within 5%, at a 95% confidence level. Laboratory experiments for dynamic leaching of the uranium ore were carried out in mechanically agitated beakers and Buchner funnels were used for solid/liquid separation.

A Pilot plant scale of dynamic leaching experiments was carried out in a 10 liters cylindrical stainless steel vessel with a vapor heating system and mechanical agitation. Dried ground ore, concentrated sulfuric acid, scrubbing water, and Caro's acid (used as oxidant) were continuously fed into the vessel.

Caro's Acid (H_2SO_5), was prepared according to the Interlox Chemicals Ltd. instructions, using 98 wt% H_2SO_4 and 50 wt% H_2O_2 , in the $\text{H}_2\text{SO}_4:\text{H}_2\text{O}_2$ molar ratio of 3:1. Under these conditions a Caro's acid containing 26 wt% H_2SO_5 , 58 wt% H_2SO_4 and 2 wt% H_2O_2 was obtained. All reagents used were of P.A type and their respective solutions were prepared with distilled water.

Uranium ore sample ground to 590 μ top size (28 mesh Tyler) was supplied by INB. The ore sample chemical characterization is shown in Table 1.

Table I – Chemical Characterization of the Ore Sample

Species	Content (wt%)	Species	Content (wt%)	Species	Content (wt%)
Moisture	< 0.01	V_2O_5	0.15	MnO	0.10
L.I. 500°C (*)	0.12	Al_2O_3	13.6	ZrO_2	0.12
L.I. 900°C (*)	0.52	Fe_2O_3	7.0	MgO	2.75
U_3O_8	0.343	P_2O_5	0.05	Na_2O	7.5
SiO_2	58.1	CaO	5.38	K_2O	0.92
TiO_2	0.42	SO_4^{2-}	0.52	Y_2O_3	< 0.01

(*) L.I = Loss of Ignition

3. RESULTS AND DISCUSSION

3.1. Batch Experiments

In this step, the influence of acid to ore ratio, oxidant to ore consumption ratio, reaction time, percentage of solids in the ground ore pulp, ore particle top size, and temperature were investigated.

Acid/ore ratio

The influence of acid to ore ratio was investigated from 20 to 50 kg/t using sodium chlorate (NaClO_3) with an ore ratio of 0.6 kg/t and H_2O_2 30 wt% with an ore ratio of 22 kg/t as oxidants. The results are shown in Figure 2. Uranium recovery was

similar for both oxidants. An analytical error of 5% corresponds with to a recovery error of approximately 0.5%. The recovery increased from (86 ± 1) to (89 ± 1) % when the acid to ore ratio increased from 20 to 50 kg/t (Fig. 1).

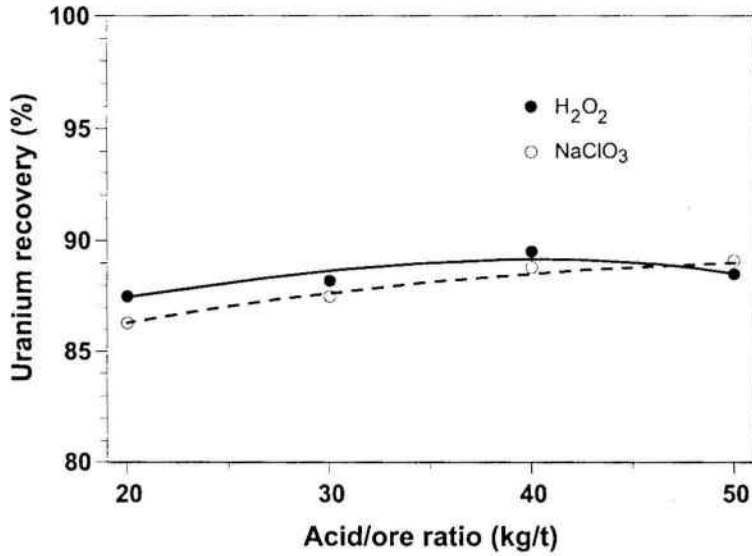


Figure 1. The influence of acid to ore ratio on uranium recovery using NaClO₃ and H₂O₂ as oxidant. Fixed parameters: temperature 70°C, leaching time 4h, ore top size 590 μ, and percentage of solids 70 wt%.

Temperature:

The temperature influence on uranium dissolution was investigated from room temperature (30°C) to 70°C. The experiments were carried out with acid to ore ratio of 30 kg/t, leaching time 4h, ore top size 590 μ, 70 wt% pulp density, and using NaClO₃ as oxidant. The temperature effect on uranium recovery in leaching step is presented in Figure 2. As it is shown the uranium recovery increases with the temperature. The temperature used for the remaining of the work was 70°C.

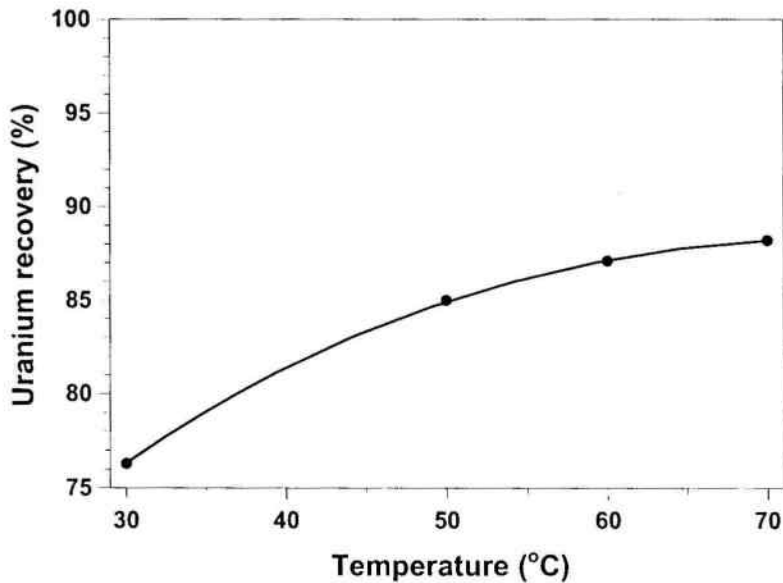


Figure 2. Influence of temperature on uranium recovery. Fixed parameters: acid to ore ratio of 30 kg/t, leaching time 4 hours, ore particle top size 590 μ, percentage of solids 70 wt%, and 0.6 kg/t NaClO₃.

Oxidant

Sodium chlorate is generally the oxidant used in uranium ore leaching, and is the oxidant used in UCP. In the UCP process, all aqueous effluents are recirculated after lime treatment until a pH of 9 is achieved. As the chloride ion was not removed by this treatment, the chloride content in the liquor has increased, decreasing the uranium extraction efficiency (Morais et al., 2005; Morais and Gomiero, 2005). This work investigated the effects of some other oxidants on uranium ore leaching, which were aiming to replace the NaClO_3 . The oxidant agents on uranium recovery investigated were: NaClO_3 , H_2O_2 30%, oxygen bubbling, air bubbling, ozone bubbling, and Caro's acid (H_2SO_5). The fixed conditions were: pulp solids percent 70 wt%, acid/ore ratio 30 kg/t, temperature 70°C , ore top size $590\ \mu$, and a leaching time of 4 hours.

The results are shown in Table II. Oxygen and air bubbling in the ore pulp have no influence on uranium recovery. The best result was obtained with Caro's acid addition. It is probably due to the increase of the final free acidity when this oxidant is used.

Table II - Influence of oxidant type on uranium recovery

Oxidant	Oxidant/ore ratio	Pulp redox potential (V)*	U recovery (%)
NaClO_3	0.6 kg/t	0.520	87.5
H_2O_2 30 wt%	22 kg/t	0.530	88.2
O_2	-	0.410	58.5
Air	-	0.410	55.2
Ozone	-	0.420	59.6
H_2SO_5 25 %wt	22 kg/t	0.550	91.3

* The redox potential was measured with a Pt electrode using a saturated Ag-AgCl as the reference electrode. The potential of the reference electrode was not considered.

Leaching time

The influence of leaching time on uranium recovery was investigated in the interval between 2 to 5 hours. Results are shown in Figure 3. In the time interval investigated, the uranium recovery was not substantially affected. When the leaching time increases from 2 to 4 hours, the uranium recovery rises from 90% to 92%, maintaining this last value with 5 hours of leaching.

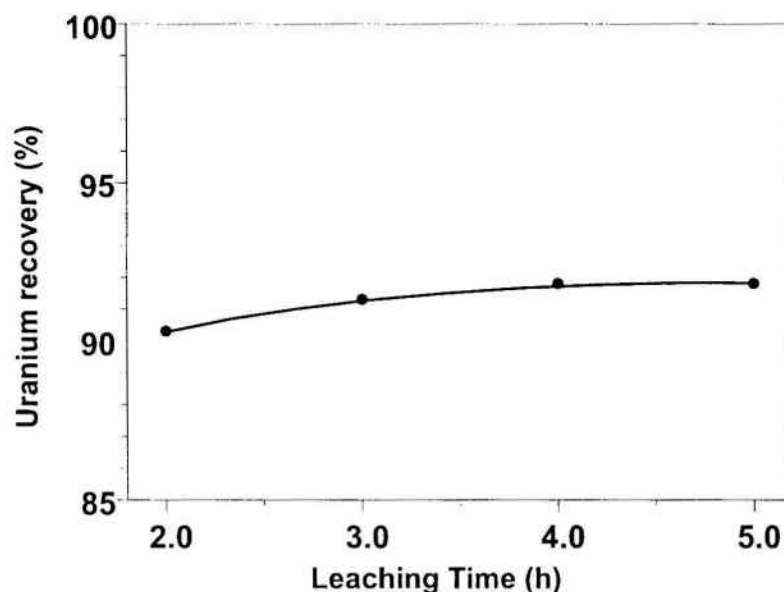


Figure 3. The influence of leaching time on uranium recovery. Fixed parameters: temperature 70°C , acid to ore ratio 30kg/t, ore top size $590\ \mu$, percentage of solids 70 wt%, and oxidant H_2SO_5 .

Percentage of solids

The solids content in ore pulp was investigated from 60 to 70 wt%. In this interval, no influence on uranium recovery was observed. High solids content in the ore pulp is important to maintain the suspension of the ore particles during the dynamic leaching process.

Ore particle size

The influence of the ore particle size on uranium recovery was investigated at 3 top sizes: 590 μ (28 mesh Tyler), 297 μ (48 mesh Tyler), 148 μ (100 mesh Tyler), and 105 μ (150 mesh Tyler). The experiments were conducted while maintaining the following conditions: leaching time 4h, temperature 70°C, acid to ore ratio 30 kg/t, 70 wt% pulp density, and oxidant H₂SO₅. The results are shown in Figure 4. An important increase on uranium recovery can be observed as the ore particle size decreases. It is due to the increased uranium mineral availability to the acid attack. When the ore top size reduces from 590 μ to 105 μ , the uranium recovery increases from 91.8% to 98.6%, resulting in 96.5% and 97.8% recovery for the ore top sizes of 297 μ and 148 μ respectively. The decision about the ore particle size to be adopted depends on the economical assessment of the investment on mill assembly, and the turn over considering the price of uranium.

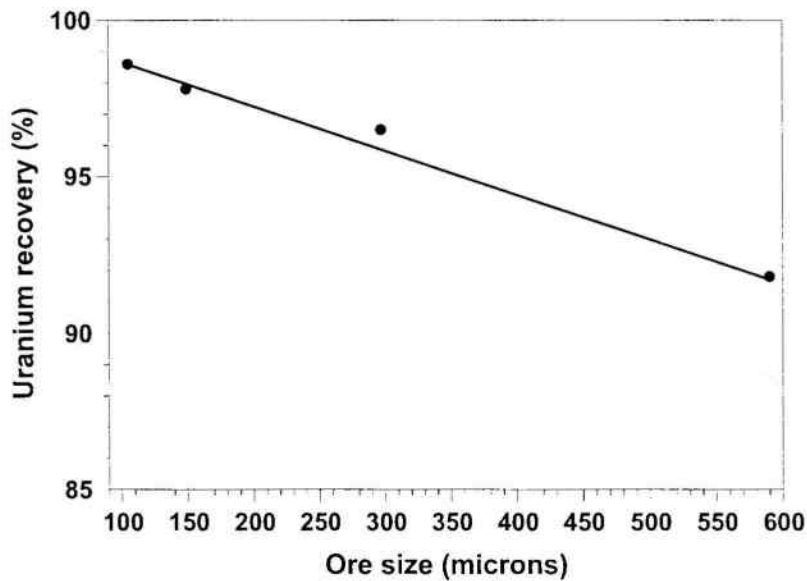


Figure 4. The influence of the ore particle size on uranium recovery. Fixed parameters: temperature 70°C, acid/ore ratio 30kg/t, percentage of solids 70 wt%, oxidant H₂SO₅, and leaching time 4 hours.

3.2 Continuous Experiments

36-hours of continuous experiments were undertaken in a 10 L stainless steel reactor under the following conditions: ore top size 590 μ , temperature 70°C, solids percent 65 wt%, acid/ore ratio 28,5 kg/t, oxidant/ore ratio 22 kg Caro's acid/t (4 kg H₂O₂ 50 wt% per ton of ore), and average pulp flow 2.45 L/h.

Average U₃O₈ content in solid phase (washed leached ore) of pulp samples taken hourly from the overflow of the leaching reactor was 0.020 wt%, which means a substantial uranium recovery of approximately 94%. This recovery is approximately 20% greater than the 75% historical uranium recovery obtained by heap leaching. Despite the increase in the acid and oxidant consumption (40% for acid and 100% for oxidant considering NaClO₃ instead of Caro's acid), it can be advantageous to change from the method of heap leaching of crushed ore to the method of dynamic leaching of ground ore.

When comparing heap leaching with dynamic leaching an additional amount of uranium recovery as U_3O_8 from one year from the milling of 180,000 tons of ore containing 0.29 wt% U_3O_8 would be about 100 tons. It means approximately 220,000 pounds and amounts to approximately US\$ 18 million.

4. CONCLUSION

Dynamic leaching demonstrated better uranium recovery than heap leaching for the uranium ore in Caetité, BA - Brazil. The most important variables in dynamic leaching are the ore particle size, the temperature, and the ore oxidation. Caro's acid, a mixture of sulfuric acid and hydrogen peroxide, proved to be the best of all the oxidants investigated. Depending on the ore top size, the uranium recovery in the dynamic leaching step can be greater than 98%.

5. ACKNOWLEDGEMENTS

The authors would like to acknowledge the CDTN's technicians that were involved in this work, especially Eugênio M. Oliveira, Francisco A. Souza, José dos Santos J. Pereira, Marcos A. Evangelista, Liliane P. Tavares and Luiz C. Silva.

6. REFERENCES

Gomiero, L.A. Uranium Production in Caetité, Brazil. Proceedings of the Regional Technical Meeting "Uranium Exploration, Mining, Production, Mine Remediation and Environmental Issues", Mendoza, Argentina, 2006, International Atomic Energy Agency edition, in press.

Interox Chemicals Ltd. Caro's Acid Laboratory Procedure for Hydrometallurgy. Report A O.5.5

Morais, C. A. e Gomiero, L. A. Uranium Stripping from Tertiary Amine Loaded Solution by Ammonium Sulfate. Minerals Engineering, v. 18, p. 1277-1281, 2005

Morais, C. A., Gomiero, L. A., Scassiotti Filho, W. e Rangel Junior, H., Uranium Stripping from Tertiary Amine by Sulfuric Acid Solution and its Precipitation as Uranium Peroxide, Minerals Engineering, v. 18, p. 1331-1333, 2005.

Morais, C.A., Ciminelli, V.S.T. Europium recovery by photochemical reduction from Eu and Eu-Gd Chlorid solutions, Sep. Sci. Technol., v.37 (14), p. 3305-3321 (2002).

Matos, E.C. e Rubini, L.A. Reservas Brasileiras de Urânio e sua Capacidade de Atendimento à Demanda Interna. VII Congresso Geral de Energia Nuclear, Belo Horizonte, Brasil, 1999.

