Desalination and Water Treatment
www.deswater.com
doi: 10.1080/19443994.2013.808792

52 (2014) 407–414
January

Taylor & Francis
Taylor & Francis Group

Application of cavitation in uranium leaching

Y.S. Ladola[a,b,*], S. Chowdhury[a], S.B. Roy[a], A.B. Pandit[b]

[a]*Uranium Extraction Division, Bhabha Atomic Research Centre, Mumbai 400085, India*
Tel. +91 22 25595696; email: mrsued@barc.gov.in
[b]*Chemical Engineering Department, Institute of Chemical Technology, Matunga, Mumbai 400019, India*

Received 17 April 2012; Accepted 10 February 2013

ABSTRACT

Cavitation is mostly considered as an operational problem and not desirable phenomena. The rapid creation and collapse of bubbles can destroy pump and erode other equipment. Recently, cavitation has been explored to enhance mass transfer and also to enhance or alter chemical reactions. Cavitation by definition is the formation, growth and rapid collapse of bubbles. Cavitation can be generated by different techniques. Hydrodynamic (hydraulic) and acoustic cavitations are the results of overcoming the tension existing in a liquid using fluid and sound energy, respectively. Optic, charge particle and steam bubble cavitations are the consequence of local deposition of energy using light, high energy elementary particles beam and steam bubble, respectively. For industrial application, hydrodynamic and acoustic cavitations are more important. Steam bubble cavitation is a recent invention and is a highly promising candidate for industrial applications in future. Improvement in recovery and enhancement in rate of recovery during leaching by ultrasound is documented in literature. Uranium leaching from carnotite ore with ultrasound was reported in 1968 by Russia and ultrasonic leaching of urania impregnated in graphite fuel was reported in 1961 by the USA. There is no other published literature available on uranium leaching with cavitation. However, lot more research has been carried out under sonochemistry for process intensification. Different types of cavitation reactor schemes are proposed by researchers for the process intensification. In this paper, we have reviewed uranium leaching with cavitation using different cavitation mechanisms. Effect of cavitation-aided leaching of uranium from MgF_2 has been experimentally established. Uranium leaching of Narwapahar ore with acoustic and hydrodynamic cavitation also has been studied.

Keywords: Uranium; Leaching; Cavitation; Process intensification

1. Introduction

The conventional way of processing of uranium ore and secondary resources is through hydrometallurgical route in one of the two ways, acid leaching or alkali leaching, depending on the ore characteristics. Uranium is solubilized in almost every case by leaching the ground source with dilute sulphuric acid or with sodium carbonate–bicarbonate mixture. The history of the sulphuric acid leaching process dates back only from 1944, when the researchers at the Massachusetts Institute of Technology working on the

*Corresponding author.

Presented at the DAE—BRNS Biennial Symposium on Emerging Trends in Separation Science and Technology (SESTEC 2012) Mumbai, India, 27 February–1 March 2012

treatment of low grade uranium ores hit upon this method. Since then, chemistry of the process has been well understood and several variations of the original method have been worked out to suit particular ores.

In India, presently two uranium mills working at Jaduguda and at Turamdih are processing uranium by using indigenously developed acid leaching method. For the ore of Tummalapalle deposit, which is with carbonate host rock, carbonate–bicarbonate leaching process has been developed and the mill is in commissioning stage. However, till today sulphuric acid leaching is the most commonly used uranium leaching method in the world.

Sulphuric acid has a major advantage that it produces anionic uranyl sulphate complex, which makes its separation easy from other cationic gangue mineral in subsequent anion type ion exchange compared to nitric acid or hydrochloric acid. Kinetics of carbonate leaching is slow and it requires fine grinding and high temperature to achieve reasonable leaching rate. Importance of uranium mining and extraction has changed with time as uranium found its application in different fields, since its discovery in 1789. Earlier thrust was on rich ore processing. However, increase in demand of uranium has extensively pushed for low grade uranium processing. For maximum utilization of available resources, new techniques of uranium processing have been tried on lean ores [1]. Application of cavitation in the leaching is also a process intensifying effort.

Cavitation by definition is the formation, growth and rapid collapse of bubbles. When liquid is irradiated with acoustic wave, different phenomena occur simultaneously. It has been understood that ultrasonic wave below 1 MHz frequency generates cavitation under normal condition. Generally, cavitation is considered as an operational problem and not desirable phenomena in chemical industry, as it can destroy pump and erode other rotating equipment of turbo machinery. However, controlled generation of cavitation with ultrasonic wave or by other means can be useful for process intensification. Cavitation has been exploited to enhance mass transfer and enhance or alter chemical reactions.

The hotspot theory postulates that when the bubble collapses in a liquid medium localized hotspot is formed. Temperature and pressure of hotspot go up to 10,000 K and 1,000 bar, respectively, and free radicals are formed. If solid surface is close to collapsing cavity, micro jet of liquid is formed and impinges on the solid surface. Velocity of micro jet is in the range of 300 m/s. [2]. Shock wave also propagates during collapse of bubbles causing acoustic streaming and local fluid turbulence generation.

$$U^{+4}_{(s)} + 2Fe^{+3}_{(aq)} \longleftrightarrow U^{+6}_{(aq)} + 2Fe^{+2}_{(aq)} \quad (1)$$

Leaching of uranium from ore is an electrochemical reaction, as tetravalent uranium converts to hexavalent uranium by ferric ion and hexavalent uranium gets dissolved in acidic leach solution. Present work was conducted to observe the effect of acoustic cavitation on sulfuric acid leaching of Narwapahar ore and extraction of uranium from MgF_2 slag material.

2. Generation of cavitation and its use in uranium leaching

Cavitation can be generated using different techniques like hydraulic or hydrodynamic, acoustic, steam bubble, charge particle and optical. Hydrodynamic (hydraulic) and acoustic cavitations are the results of overcoming the liquid tension existing in a liquid using fluid and sound energy, respectively. Optic, charge particle and steam bubble cavitations are the consequence of local deposition of energy using light, high energy elementary particles beam and steam bubble, respectively, as shown in Fig. 1.

For industrial application, hydrodynamic and acoustic cavitations are more important. Steam bubble cavitation is a recent invention and is a highly promising candidate for industrial applications in the future.

Basic steps in the cavitation phenomena are:

(1) Break in the cohesive forces in the liquid continuum—formation of voids.
(2) Growth of voids with continual supply of energy.
(3) Collapse of the void (cavity) on removal of energy source.
(4) Release of the total energy supplied over steps 1 and 2 during the implosive collapse of the fully grown cavity.

Important effects of cavitation from reaction point of view are:

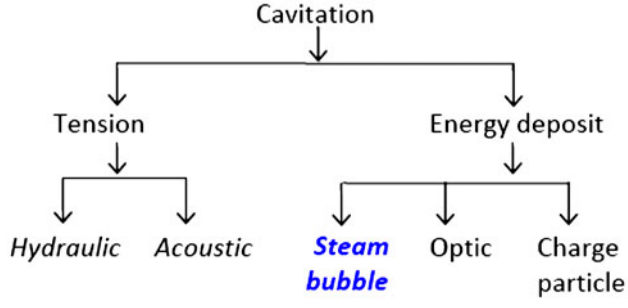

Fig. 1. Different techniques of cavitation.

(1) Generation of local high temperature and pressure, useful for reaction rate enhancement and enhancement of transport properties.
(2) Shock wave generation during cavity collapse decreases thickness of boundary layer in solid–fluid reaction or solid–liquid mass transfer resistance.
(3) Micro-jet impinging on solid either fragments or cracks the particle, ultimately exposing larger surface area for reaction.
(4) Formation of free radicals enhances nucleophilic reactions.

All these effects can be exploited for the enhancement of mass transfer, rate of reaction and improvement in the overall yield of the physico-chemical transformation. Cavitational reactors have been reported for process intensification in many types of reactions [2] including fusion reaction.

Cavitation can easily be generated by ultrasound. Liquid produces cyclic tensions (expansion) and compressions as ultrasound waves pass through it. Bubbles generate and grow during tension cycle and collapse in compression cycle. Ultrasonic bath, ultrasonic horn or ultrasonic transducer generates cavitation by ultrasound and these equipments are primarily used in research. These reactors are generally called sono-chemical reactors or ultrasonic reactors in literature. Process studied by ultrasonic cavitation is generally called ultrasonic process, e.g. ultrasonic leaching. Ultrasound is generated by piezoelectric transducer or magnetostrictive transducer. Piezoelectric transducer is easy to build and relatively cheap, whereas magnetostrictive transducer is expensive but rugged. Ultrasonic cleaning bath is easily available and mostly used for study of cavitation-aided process like leaching. Poor reproducibility of ultrasonic leaching with ultrasonic bath is due to non-uniformity of cavitation activity in bath [3]. Distribution in cavitation activity varies with level of water in ultrasonic bath due to standing wave formation. This is a serious problem for ultrasonic research and scale up from laboratory study.

Ultrasonic leaching of Urania impregnated in graphite fuel was studied in the USA in 1961. They had observed that ultrasonic leaching with already ground simulated pebble graphite fuel was more efficient than non-ultrasonic leaching. Uranium content in source material was 2% and improvement of efficiency with ultrasound was found to be from 96.5 to 99.5% [4]. Ultrasonic leaching of carnotite-type ore was studied in Russia in 1968. They had observed enhancement of rate of leaching and enhancement in recovery with same sulphuric acid concentration [5].

3. Experiments

3.1. Uranium resources

In India, as nuclear fuel, metallic uranium is used in research reactors (RR) and uranium dioxide pellets are used in power reactors (PR). Source of indigenous uranium is either from underground-mined primary ore or monazite sand available on ground. Considering the potential of cavitation as process intensifier, experiment was started in BARC, Mumbai, in collaboration with ICT, Mumbai. Experiments have been carried out with two uranium resources. Uranium leaching from MgF_2, by-product of uranium metal ingot production process is studied. MgF_2 is hard and brittle solid and uranium is physically absorbed in solid matrix. Uranium content was 3–4%. Experiment was carried out for nitric acid leaching with different nitric acid concentrations. Cavitational uranium leaching study was extended to uranium ore due to the encouraging results obtained for MgF_2 leaching. Study was conducted to observe the effect of ultrasonic cavitation on extraction of uranium from Narwapahar ore. Characteristic of solid material is important for leaching. Optical microscopy of Narwapahar rock shows that uzraninite–magnetite minerals are distributed in chlorite (it is one type of mica) as shown in Fig. 2. It is important to note that sizes

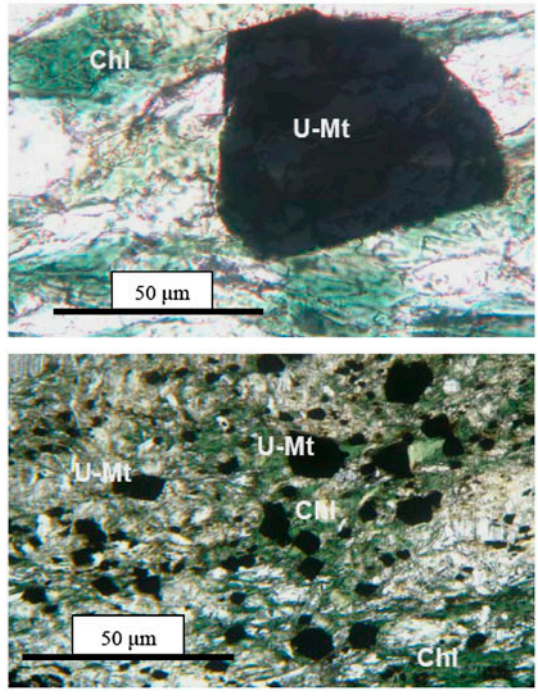

Fig. 2. Microstructure of Narwapahar ore shows uraninite–magnetite (U-Mt) grains distributed within chlorite-quartzofeldspathic.

of minerals are below 10 μm with average uranium concentration of 0.03–0.038% (w/w). This is in confirmation to the conclusion drawn by Padmanabhan et al. that uranium may be in ultrafine inclusions in mica particles [6]. There may be other possibility with ultrafine inclusion in refractory uranium mineral like brannerite. However, XRD analysis of Narwapahar ore has not confirmed any other mineral except uraninite. Brannerite has not been found in either ore sample or leach residue.

3.2. Experimental procedure

3.2.1. Uranium leaching from MgF_2

Uranium leaching from MgF_2 was performed in cylindrical round bottom glass reactor of 200 mL capacity. Reactor was kept at an optimum location inside ultrasonic bath for ultrasound irradiation. Power and frequency of ultrasonic bath were 36 W and 20 kHz, respectively. Lab agitator, six pitched blades down-pumping, was used for suspension of slurry. Slurry was prepared with 50 g of MgF_2 and 50 mL of nitric acid. Different concentrations of acid were used for study. Uranium content of MgF_2 was 3% (w/w).

3.2.2. Uranium leaching from ore

Uranium leaching experiments were conducted using acoustic cavitation with different particle size of Narwapahar ore. Mean particle size and uranium content are shown in Table 1. Experiments have been conducted under simulated plant condition in a 30-L batch reactor. Experimental set-up is shown in Fig. 3. Ore slurry of 50% solid (by weight) is prepared using 17 kg ore and 17 L water. Ore slurry is kept in suspension using four pitched blades down-pumping impeller rotating at 100 rpm in the reactor. The slurry is circulated through the ultrasonic flow cell using a piston pump at a rate of 1.5 m^3/h giving pipe slurry velocity of 0.8 m/s. Cavitation is generated by 1 kW radial ultrasonic horn arranged as a flow cell. Concentrated H_2SO_4 and laboratory grade MnO_2 are added in a controlled manner in slurry mass to maintain the required pH and oxidation—reduction potential (ORP). pH and ORP are monitored using pH and ORP probes, respectively. These probes are attached to a 2-channel display. pH is maintained at 2.0 during first 2 h of experiment and is maintained at 1.8 pH during remaining period of the experiment. ORP is maintained at 480–510 mV range during experiment. Uranium leaching experiments have been conducted using ultrasonic bath also. Ore slurry of 50% solid (by weight) is prepared using 500 g of ore and 500 mL of water. Ore slurry is kept in suspension using four pitched blades down-pumping impeller rotating at 100 rpm in 1 L beaker. Beaker was placed in ultrasonic bath for irradiation with ultrasound.

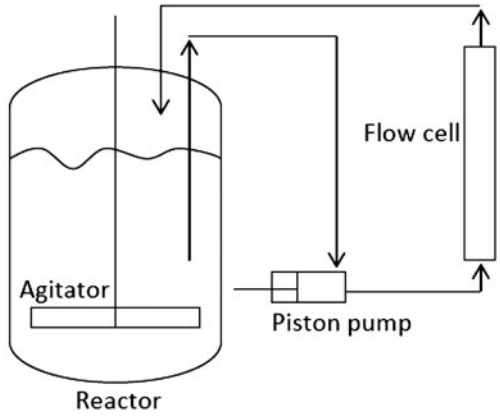

Fig. 3. Experimental set up for ore leaching with acoustic cavitation by flow cell.

Table 1
Mean particle size and uranium concentration in Narwapahar ore

Lot-1	Mean particle size (μm)	Uranium concentration (% wt.)
Ore 1	200	0.032
Ore 2	30	0.030
Lot-2		
Ore 3	50	0.038

3.2.3. Analytical methods

Uranium content in the ore and residue samples have been carried out as per the procedure followed by UCIL, India [7]. Weighed quantity of sample is digested with hydrofluoric acid–nitric acid mixture and uranium in the resultant solution is extracted with tri-n-butyl phosphate diluted with kerosene. Uranium from the organic has stripped with sodium sulphate and the solution is made alkaline with sodium hydroxide. Colour development is achieved by adding hydrogen peroxide and the absorbance of this complex is measured at 380 nm. Uranium in ore and residue is also determined using bromo-PADAP as the colour-forming reagent [8]. In this procedure, the sample is digested with a mixture of nitric acid–hydrofluoric acid and the uranium is extracted

using tri-octyl phosphineoxide diluted with cyclohexane. Colour is developed in the organic phase using 1% solution of bromo-PADAP. Absorbance measurement is carried out at 574 nm. Uranium in leach liquor is measured by spectrophometric method using dibenzoyl methane as the chromogenic reagent [9]. Uranium is extracted into ethyl acetate medium using aluminium nitrate as a salting-out agent. Absorbance measurement is carried out at 395 nm using 1 cm cells. Particle size is measured by laser diffraction particle size analyser CILAS 1180. The precision of this method is within ± 5%.

4. Results and discussions

Experiment was carried out for MgF_2 slag leaching with different nitric acid concentrations in ultrasonic bath. MgF_2 is treated with nitric acid for uranium recovery at UED, BARC; hence, nitric acid was selected for MgF_2 leaching study. Uranium recovery with time is shown in Figs. 4–6 for with and without ultrasonic cavitation in different nitric acid concentrations. In this work, improvement in uranium leaching rate and uranium recovery have been observed due to ultrasonic cavitation as shown in Table 2. This improvement is due to significant particle size reduction as shown in Fig. 7 due to ultrasonic cavitation condition as well as other cavitational effect. Uranium recovery has improved more than 10% for same acid concentration. Reduction in nitric acid concentration is possible with cavitation which may subsequently reduce nitrate waste.

Uranium recovery for ore-1 with and without ultrasonic condition is 67 and 60%, respectively. Rate of leaching is faster in the case of ultrasonic cavitation condition. Uranium recovery for ore-2 in ultrasonic condition is 69%, whereas it is 67% for without ultrasonic condition. Uranium recovery with time is shown in Fig. 8 for with and without ultrasonic cavitation. Large difference in final recovery for ore-1 is due to considerable particle disintegration in larger size ore (ore-1) material. All particles above 100 μm are disintegrated to smaller size as shown in Fig. 9. Smaller size (30 μm) ore particles (ore-2) have not shown significant disintegration; this is the reason for marginal difference in uranium recovery. This can be explained based on size of collapsing bubble due to cavitation. Generally size of collapsing bubble in

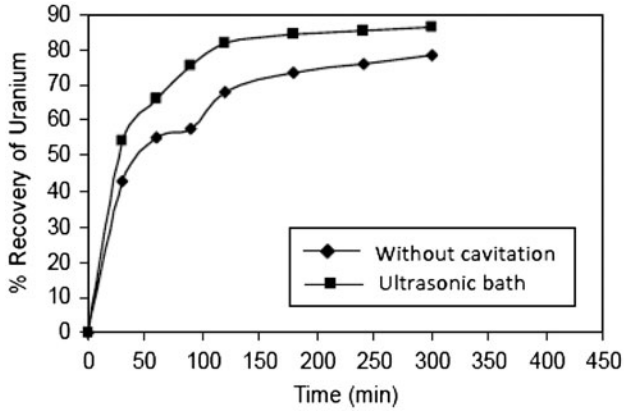

Fig. 4. Leaching of MgF_2 slag with 10% (v/v) nitric acid.

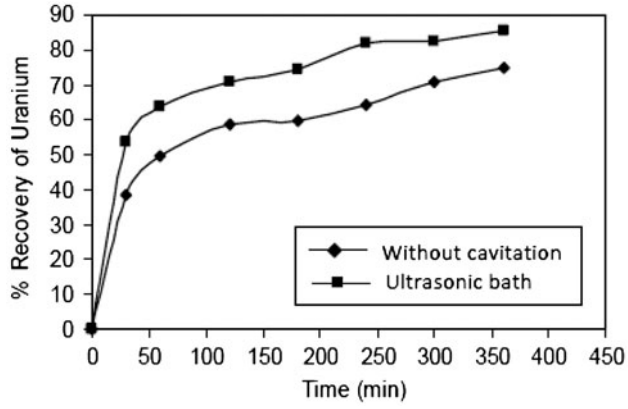

Fig. 5. Leaching of MgF_2 slag with 7.5% (v/v) nitric acid.

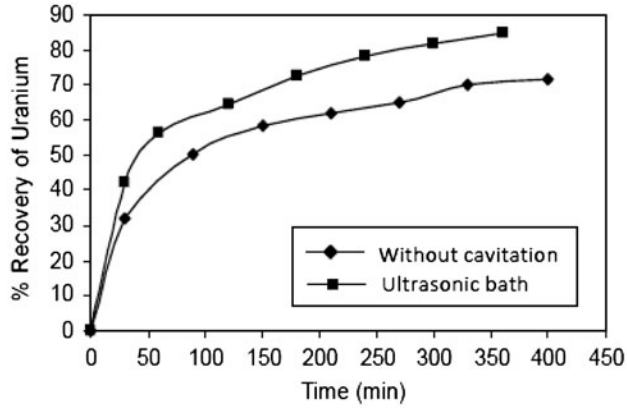

Fig. 6. Leaching of MgF_2 slag with 5% (v/v) nitric acid.

Table 2
Uranium recovery from MgF_2 slag

Nitric acid concentration (% vol.)	% Uranium recovery	
	Without cavitation	With cavitation
5	72	84
7.5	75	85
10	78	87

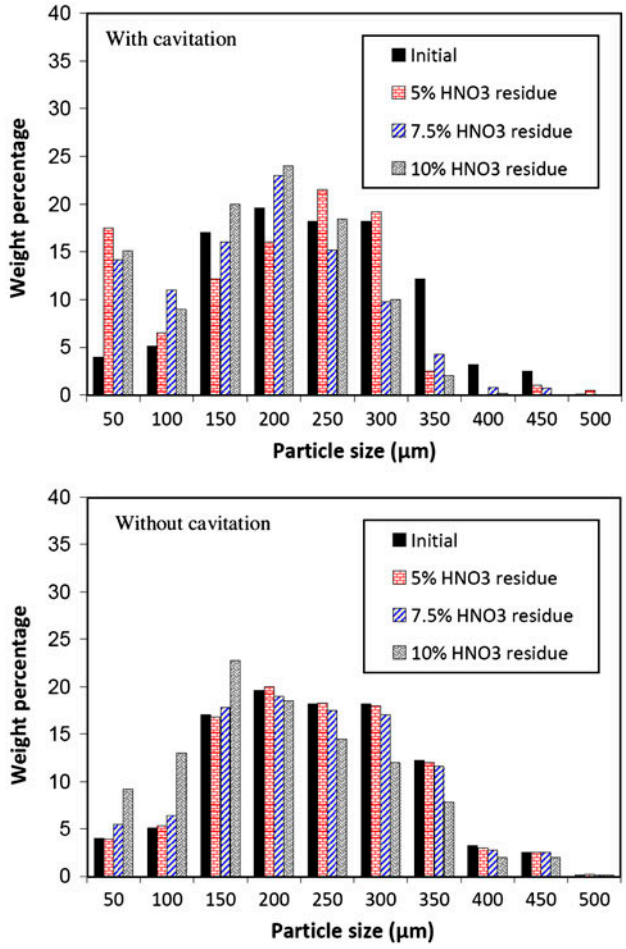

Fig. 7. Particle disintegration of MgF_2 with and without cavitation.

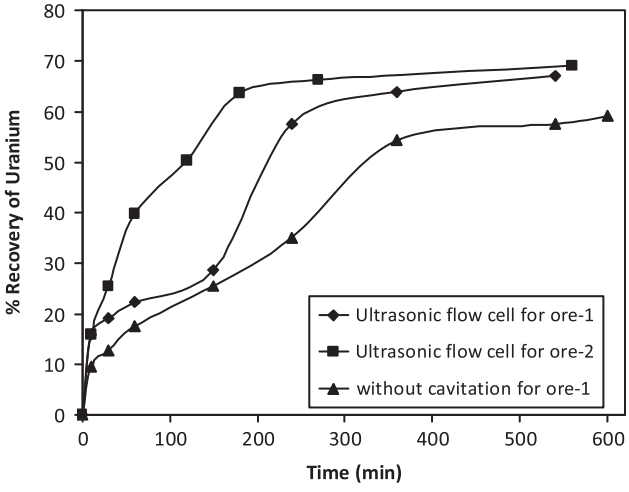

Fig. 8. Leaching of Narwaphar ore in ultrasonic flow cell and without cavitation.

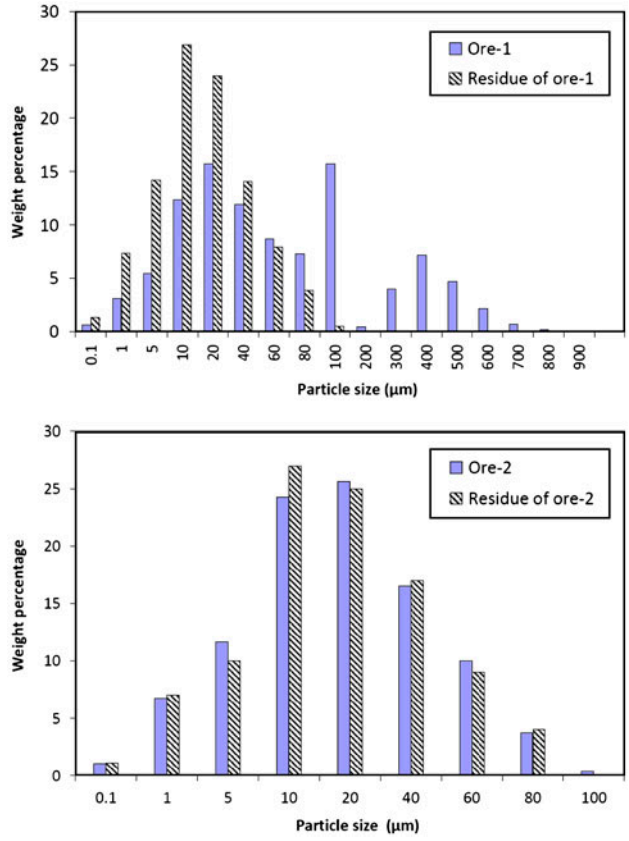

Fig. 9. Ore particle disintegration during acoustic leaching.

water by 20 kHz ultrasound irradiation is reported to be in the range of 40–120 µm [2]. If size of the bubble is in the range of particle size then micro-jet of liquid formed due to bubble collapse cannot impinge on the particle and then particles smaller than bubble size are not disintegrated. Larger size particles (200 µm) break up till they reach the size about same as that of the collapsing bubble size range. For ore-2, scanning electron microscopy (SEM) was conducted for both ore and leach residue material after ultrasonic cavitation leaching. SEM photograph has been shown in Fig. 10. Although particle erosion has been observed on residue particles, no fractured surface has been observed in SEM micrograph. Initial rate of leaching is slower in case of ore-3 compare to ore-1 and ore-2. This may be due to the different nature of ore, because ore-1 and ore-2 are from the same lot of materials whereas ore-3 is from a different lot of material. Leaching curve for ultrasonic bath, ultrasonic flow cell and without sonic effect is shown in Fig. 11. Uranium recovery is almost same for all three cases for ore-3. Uranium recovery is 74% for ultrasonic bath and ultrasonic flow cell, whereas for without it is 71%. Rate of leaching is faster for ultrasonic cavitation

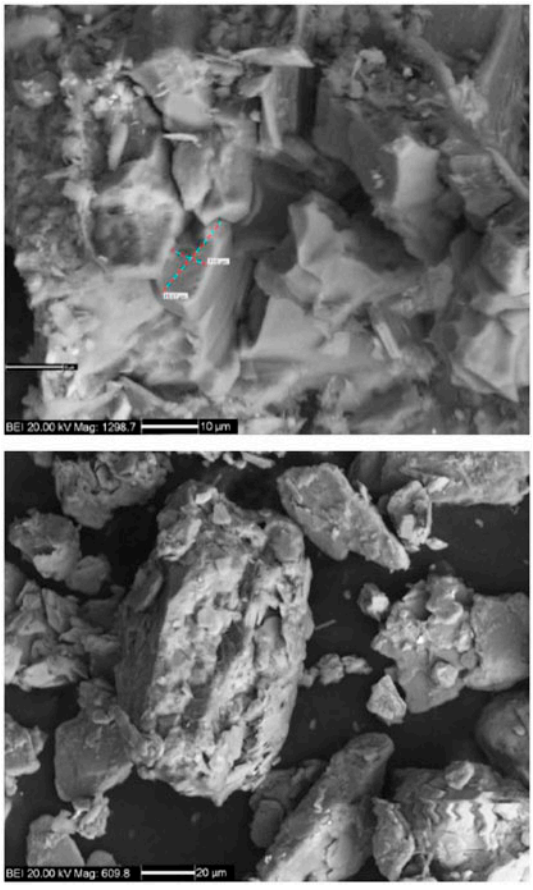

Fig. 10. Scanning electron micrograph of ore particles before and after acoustic leaching.

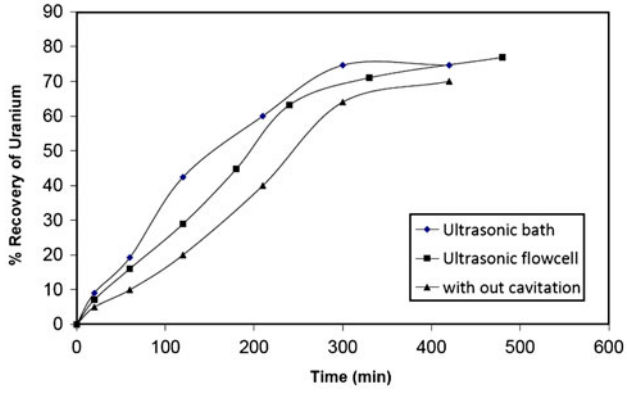

Fig. 11. Leaching of uranium ore, where mean size of the particle is 50 µm (ore-3).

conditions due to particle disintegration with time as shown in Fig. 12. Particles above 100 µm disintegrated to smaller size similar to ore-1. Enhancement of recovery in cavitational leaching depends on characteristics of solid matrix. Below the critical particle size,

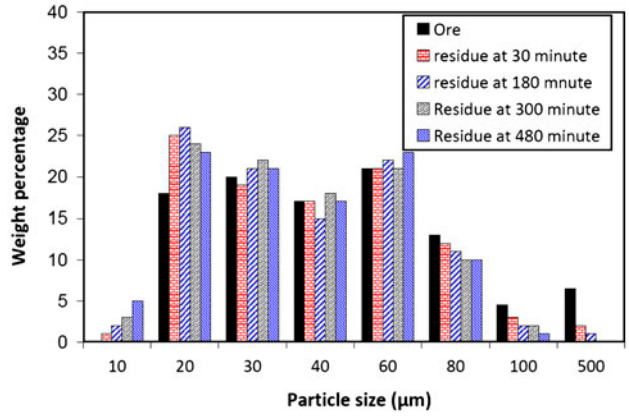

Fig. 12. Particle size distribution for different time in ultrasonic leaching with flow cell for ore-3.

cavitational leaching does not have much effect in leaching recovery but it can improve leaching rate [3] as we have observed in Narwapahar ore.

5. Conclusion

Improvement of uranium recovery has been observed for MgF_2 slag in ultrasonic leaching, due to significant particle size disintegration and other cavitational effect. Effect of acoustic cavitation is greater on larger size ore particles and significant particle size disintegration has been observed for larger size ore particles. It has been observed that particle size disintegration occurred up to the particle size where they nearly reach the size of collapsing bubbles. Effect of cavitation depends on the characteristics of solid matrix. Further study in cavitational leaching for uranium with different ores may be beneficial. Below critical particle size cavitational leaching do not have much effect in leaching recovery but it can improve leaching rate.

Acknowledgement

The authors wish to acknowledge the Quality Control Section, UED, BARC, for their analytical support. First author would like to thank Dr A. Balasubrahmanyam for his help.

References

[1] Y.S. Ladola, S.V. Kadam, K.N. Hareendran, S. Chowdhury, S. Biswas, S.B. Roy, A.B. Pandit, Uranium balancing in Narwapahar Ore leaching presented in ChemCon 2010 at Annamalai University, Annamalai Nagar, December 2010.
[2] Balasubrahmanyam Avvaru, Cavitation Phenomena in Heterogeneous System: Intensification in Localized Transport. PhD thesis, ICT (UDCT), Mumbai, 2009.

[3] K.L. Narayan, K.M. Swamy, K.S. Rao, J.S. Murthy, Leaching of metals from ores with ultrasound, Miner. Process. Extr. Metall. Rev. 16 (1997) 239–259.
[4] W. Tarpley, R.S. Winchester, Ultrasonic Leaching of Urania-impregneted Graphite Fuel, Report No 9581, April 1961 (unclassified).
[5] V.S. Shastri, D.J. Mackinnon, Some effects of ultrasonic and their applications in metallic ore processing, J. Sci. Ind. Res. 36 (1977) 379–385.
[6] N.P.H. Padmanabhan, T. Sreenivas, Utility of process mineralogy in ore processing, J. Mineral. Soc. India 44(1) (2010) 236–257.
[7] Departmental Quality Control Manual, UCIL/DQM/CR&D/ANALYSIS.
[8] T.M. Florence, D.A. Jhonson, Analytical procedure for determination of uranium, Anal. Chim. Acta 53 (1971) 73–79.
[9] Analytical techniques in uranium exploration and ore processing, IAEA TecDoc 314 (1992).