NOVEL METHOD FOR RECYCLE OF SINTERED UO_2 REJECTED PELLETS

A.L.V.KUMAR REDDY, E. VENKATESHAM, C.RADHAKRISHNA, S.M.RAO,
U.C.GUPTA AND C.GANGULY

Nuclear Fuel Complex
Department of Atomic Energy
Hyderabad, India.

ABSTRACT

In the process of production of UO_2 pellets for PHWR fuel, some quantity of sintered pellets gets rejected due to various defects. The earlier processes of recycling these sintered rejects, like oxidising the sintered rejects to U_3O_8 and adding to the regular stream of U_3O_8 or oxidising the sintered rejects to U_3O_8 and dissolving in nitric acid, etc. This process suffers from several drawbacks like poor quality of finished product and other associated problems like air borne activity. The present process, developed and established by the authors, is an excellent method for recycling of the sintered rejects, which is environmental friendly, most economic, simple and consumes less chemicals. The present paper discusses the several stages followed in developing to the present stage and the process in detail.

1.0 DETAILS OF THE PROCESS:

In the process of making UO_2 pellets for CANDU fuel, some quantity of sintered pellets gets rejected because of defects like end cap, cracks, chips and pits. Earlier these sintered rejects were oxidized to U_3O_8 and were added to the process streams. This route resulted in powders with hard particles which required grinding and blending and was associated with problems of airborne activity due to handling of fine powders. This also resulted in powders with high molybdenum since the pellets were placed in molybdenum boats during sintering stage. Although suitable process methods, equipment and literature was available for dissolution of spent fuels, there was no study done in the direction of direct dissolution of rejected sintered PHWR fuel pellets.

Study was undertaken to exploit the pellet characteristics like limited porosity, low specific porosity, low specific surface area and high density[1]. Uranium dioxide dissolved in nitric acid by the following net reaction[2].

$$UO_2 + 4H^+ + 2NO_3^- \rightarrow UO_2^{2+} + 2NO_2 + 2H_2O$$

Equation 1: $U_3O_8 + 8HNO_3 \rightarrow 3UO_2(NO_3)_2 + 2NO_2 + 4H_2O$

Equation 2: $3U_3O_8 + 20HNO_3 \rightarrow 9UO_2(NO_3)_2 + 2NO + 10H_2O$

Equation 3: $UO_2 + 4HNO_3 \rightarrow UO_2(NO_3)_2 + 2NO_2 + 2H_2O$

Equation 4: $3UO_2 + 8HNO_3 \rightarrow 3UO_2(NO_3)_2 + 2NO + 4H_2O$

Equation 3 and 4 indicate release of 38.65 g of NO_2 and 16.81 g of NO by consuming 105.9 and 70.59 g of HNO_3 per 100 g of contained uranium in oxide. However, in the presence of oxygen, it is possible to recover NO_x fumes as nitric acid.

Experiments to establish flow sheet and process parameters for safe dissolution of tonnage quantity of rejected pellets were systematically carried out to study the effect of concentration, temperature, etc. First experiments were carried out with varying concentration of nitric acid without external heating. Each time a single pellet of 28g was immersed in 250ml of nitric acid and the period of complete dissolution in hours was noted as given in Table-1.

It took 144 hours for complete dissolution in 6N, which rapidly decreased to 38 hours when acidity was 8N. Further with increase in acidity, the period of dissolution did not decrease rapidly. |This indicated that at room temperature at lower acid concentration, control on the reaction would be poor.

Then second set of experiments were carried out by dissolving UO_2 pellets of 28 g each in 250 ml 6N acid, at various temperature as indicated in Table-2.

At 35°C, the time of dissolution was 144 hours which rapidly decreased to 18.4 hours at 70°C. Semi-continuous process trials, which are described later in this paper indicated that not only time of dissolution is short, but the free acidity available in the reactor is low at higher temperatures. Based on the results, it was concluded to dissolve in dilute nitric acid at high temperature so that the reaction would always be under control and risk of run-away reaction leading to un-controllable generation of NO_x fumes would be avoided.

With a view to recover on plant scale operation, maximum acid from NO_x fumes by oxidizing and scrubbing with water, a leak tight reactor of 3000 liters was designed. As shown in Fig.1, the reactor vessel contains steam cum cooling coil for heating or cooling the reactants. Provision is made for introducing air at the bottom of the tank. No mechanical agitator is provided as the required mixing action is generated by the air/oxygen admitted at the bottom is effective and this is further aided by irrigation effect of the bubbles during reaction. A shell and tube type water cooled condenser is placed on the top of the reactor to recover the acid from vapours[3].

Literature indicates that gaseous effluents are led through packed columns counter-current to the incoming scrubbing acid feed, together with oxygen to convert nitric oxide to dioxide which is efficiently absorbed as nitric acid[4]. As the use of oxygen involves extra expenditure, experiments were carried out by admitting air into reaction tank. Different quantities of pellets were added to 2000 liters of 6N acid in the reaction tank. Acid consumption and dissolution period for different batch sizes were noted as indicated in Table-3.

In this experiment, it was observed that dilute nitric acid generated micro bubbles while reacting with pellets. These micro bubbles containing NO_x fumes were immediately oxidized by the oxygen of the air which in turn produced nitric acid in the presence of water. As the batch size increased, the reaction time and acid consumption decreased. Even air purging resulted in almost complete recovery of NOx fumes as nitric acid and acid consumption was close to 2 mole per mole of UO_2.

To make the operation intrinsically safe, experiments were done on semi-continuous basis. All the pellets were added initially. The water required for dilution of 12N commercial acid to 6N was also added to the tank along with pellets and the 12N acid was added to the reaction vessel continuously over the period of reaction. In an experiment as shown in Fig.2, 2436 kgs of pellets and 1578 liters water were taken in the reactor. The contents were heated to 70°C and 12N acid was added at an uniform rate over a period of 24 hrs. Results indicated that dissolution rate has increased to 120 kg/hour and the temperature went up to a maximum of 80°C after 12 hours and the temperature was 70°C by the time reaction was over. Free acidity of the solution was about 0.2N throughout the reaction period indicating that the reaction can be stopped at any moment of time by stopping acid addition making the system highly controllable. To make the dissolution arrangement still safer, a pressure release limb dipping in a 3000 mm water column was introduced to avoid pressure exceeding beyond 3000 mm WG in the reactor.

This process has decreased the man power requirement and eliminated the need of grinding, blending operations (Fig.3) and minimizing the air activity for producing the acceptable quality powder.

2.0 REFERENCES:

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3. JOHN.FLAGG(ED).F, Nuclear Science and Technology, Part I, "Chemical Processing of Reactor Fuels", Chapter III, Preparation of Fuels for processing, CYRIL M. SLANSKY, (P 90).

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TABLE-1, 28g PELLETS DISSOLUTION NORMALITY Vs TIME AT ROOM TEMPERATURE

Normality of nitric acid	Period of dissolution (hours)
12	22
9	30
8	38
6	144

TABLE-2, TEMPERATURE Vs TIME OF DISSOLUTION

Temperature(°C)	Time of Dissolution (hours)
35	144.0
70	18.4
100	6.5

TABLE-3, DISSOLUTION PERIOD AND ACID CONSUMPTION FOR DIFFERENT BATCH SIZES WITH AIR PURGING

	UO_2 kgs	Dissolution Period (hours)	HNO_3 Consumption (moles per mole of UO_2)
1	574	20	2.23
2	686	19	2.17
3	754	18	2.09
4	908	16	2.05

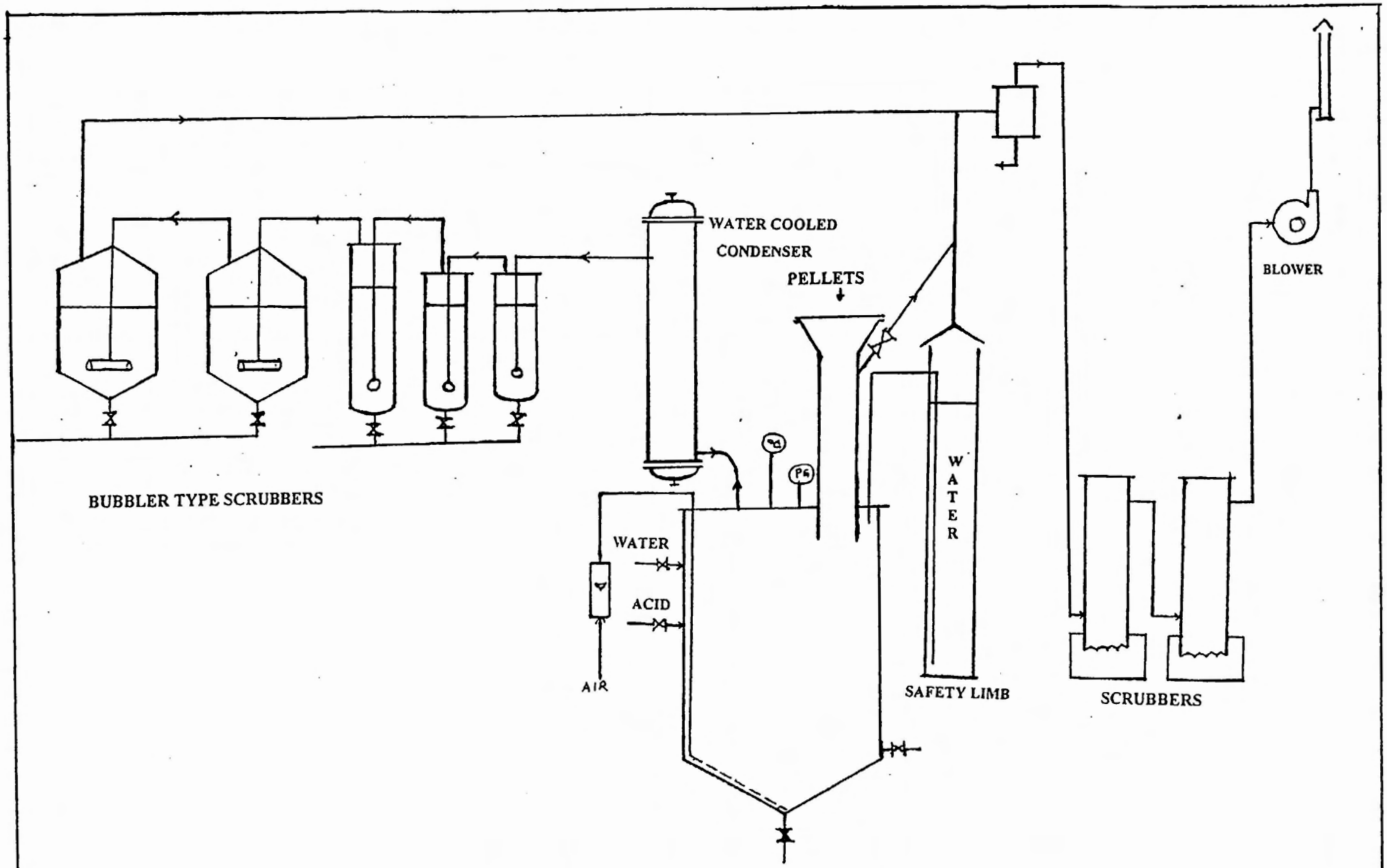

FIGURE-1 SETUP OF REJECTED PELLET DISSOLUTION

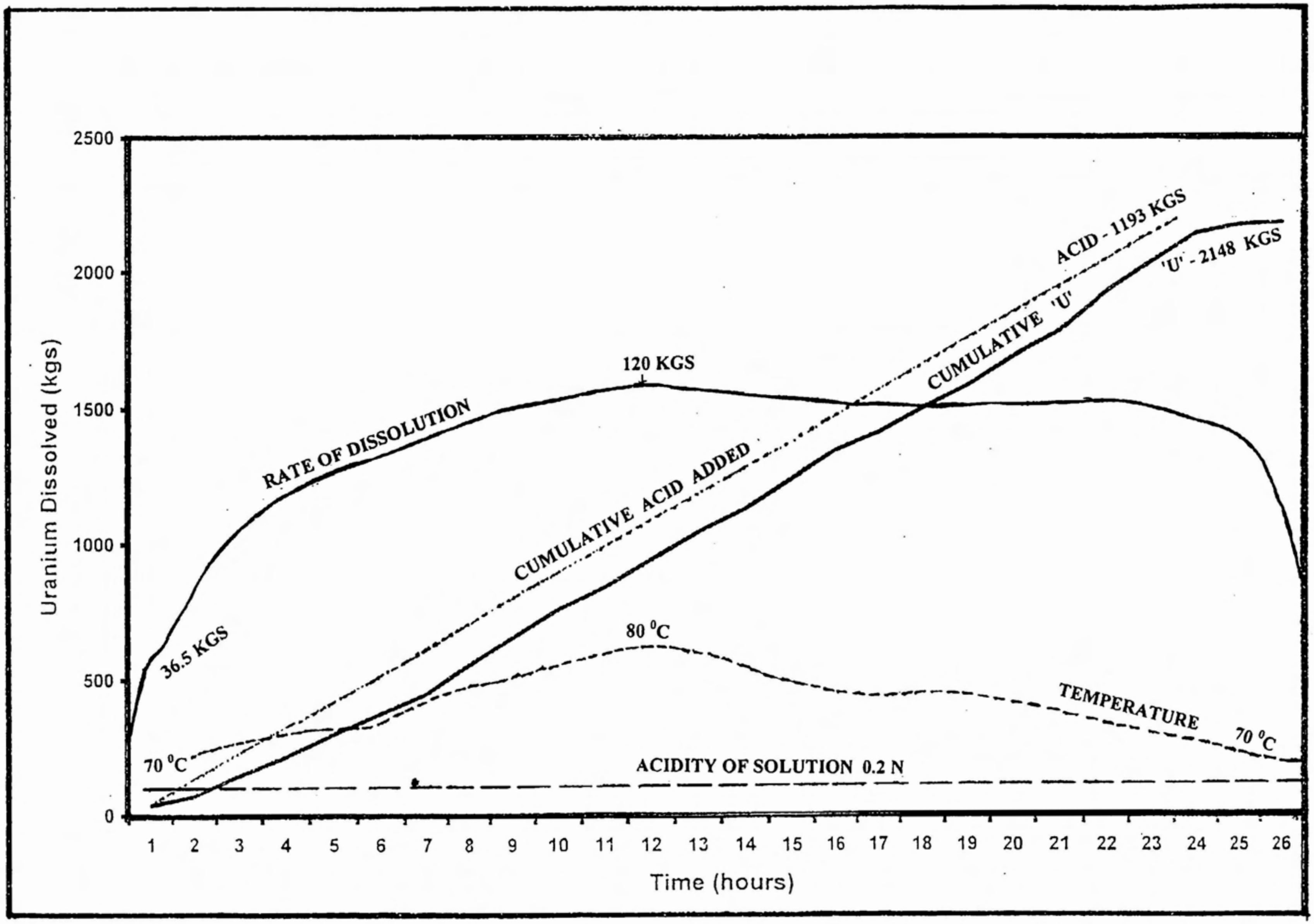

FIGURE-2 EFFECT OF TEMPERATURE AND TIME ON RATE OF PELLET DISSOLUTION (SEMI BATCH PROCESS)