DEVELOPMENT OF A PULP PROCESS FOR TREATING CONTAMINATED HEPA FILTERS (II)

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ABTRACT

The current Filter Leaching System (FLS) has operated at Idaho National Engineering and Environmental Laboratory (INEEL) since 1995 to treat very radioactive, mixed waste High Efficiency Particulate Air (HEPA) filters. The process treats the whole filter unit with filter media and calcine particles confined in the heavy filter housing. The housing causes poor mass transfer and inefficient liquid-solid separation during leaching and washing. In order to improve the efficiency of FLS, a Pulp Process (PP) has been proposed. In this process, the filter media and the trapped calcine particles are separated from the filter housing and treated as a pulp. Chemical dissolution, physical separation or both could be used to clean the contaminated filter media.

To prove the advantages of the Pulp Process, laboratory tests were performed to search for the optimum operating conditions. In a prior study, we have surveyed six different dissolution reagents (nitric acid, oxalic acid, sodium formate, Corpex 921, Turco 4502, and Turco ARR). Among them, nitric acid is the most effective reagent.

In this study, the effects of nitric acid addition order and reaction temperature were investigated. It is apparent that the acid addition orders do not affect the calcine dissolution efficiency. The results from the temperature tests indicate that heating is critical in achieving high calcine dissolution.

Under the optimum conditions, laboratory experiments were conducted to compare the Pulp Process with the current leaching system. The results of side-by-side tests indicated that the Pulp Process would significantly improve the leaching efficiency. For example, the Pulp Process increases the leaching efficiency 15-19% for aluminum calcine. For zirconium calcine, its dissolution percentage reached 97.8±0.6% in Pulp Process with nitric acid concentration of 2N, reaction time of 0.5 hour, and temperature of 88ºC.

Up to this point, the laboratory tests were conducted using shredded clean HEPA filter media mixed with non-radioactive calcine particles. Next year, hazardous-metal contaminated HEPA filters will be used. More conclusive results are expected from those tests. At the same time, laboratory plant tests will be performed to evaluate the physical separation methods.

INTRODUCTION

Current HEPA Filter Leaching System

The current Filter Leaching System (FLS) at Idaho National Engineering and Environmental Laboratory (INEEL) has been developed to treat very radioactive, mixed

waste High Efficiency Particulate Air (HEPA) filters. The FTS, built in 1988, modified in 1992 (1) and validated in 1995 (2), has treated 78 filters in 1997 and 1998.

The FTS process treats the whole filter unit with filter media and calcine particles confined in the heavy filter housing. The housing causes poor mass transfer and inefficient liquid-solid separation during leaching and washing. As a result, FLS has the following shortcomings: 1) Large volume of corrosive liquid waste generation, 2) Long cycle time, 3) Ineffective mercury removal, and 4) Lack of versatility for treating filters with different sizes.

Pulp Process

In order to improve the efficiency of the HEPA filter-leaching process, the Pulp Process (PP) was proposed. In this process, the filter media and the trapped calcine particles are separated from the filter housing and treated as a pulp. Chemical dissolution, physical separation, or both would be used in this process.

A preliminary analysis indicated that in the Pulp Process, ten filters could be treated at one batch, leaching process could be reduced from 3 cycles to 1, and the washing process could be reduced from 2 cycles to 1. Calculations based on these assumptions showed a liquid waste reduction by a factor of 25 and a cycle time reduction by a factor of 3 if the chemical dissolution is applied. If a physical separation is feasible, it is possible to eliminate the corrosive waste completely. Also, the pulp process can handle filters of different sizes and remove mercury more effectively.

Previous Laboratory Experiments

In a prior study (3,4), we have surveyed six different dissolution reagents (nitric acid, oxalic acid, sodium formate, Corpex 921, Turco 4502, and Turco ARR). Among them, nitric acid is the most effective reagent for zirconium calcine, and nitric acid and oxalic acid are the most effective reagents for aluminum calcine. The mixture of nitric acid and oxalic acid does not improve the aluminum calcine dissolution. The most effective nitric acid concentration is 2N.

Scope

Following the previous experiments, laboratory tests are performed to further search for the optimum conditions: 1) the addition order of nitric acid solution, and 2) the reaction temperature. Under the optimum condition, laboratory experiments are conducted to demonstrate the advantages of the Pulp Process over the current FLS.

EXPERIMENTAL

Materials

Two kinds of non-radioactive, bed-product calcine from pilot plant tests were used in this study: aluminum and zirconium calcines. The lot number of the aluminum calcine is RSA-1, the lot number of the zirconium calcine is R-74. The dissolution reagent, nitric acid, is of technical grade.

Apparatus and Experiment Procedure

Two sets of apparatuses were used in this study (5). One is for the pulp process tests. The other is for the tests simulating the current filter leaching process, which is named as "sandwich" process.

Pulp Process test apparatus consists of a 500-ml 3-neck flask set on a heating mantle. The central neck accommodates an overhead stirrer shaft, the second neck holds the probe of an electronic thermometer and the third one holds a condenser.

Six grams of fresh filter media shredded by a common paper shredder was blended with 3 grams of calcine particles in the flask with 250 ml of 2N nitric acid solution at a specified temperature for a specified period of time. Then the calcine residue were separated from the filter media and dried in an oven at 60ºC overnight. The calcine residue was weighed and the calcine dissolution percentage was calculated from the weights of calcine feed and residue.

"Sandwich" test apparatus is a specially designed reaction vessel. This vessel is a stainless steel cylinder with an inside diameter of 2¾" and a total height of 7". A 16-mesh screen is welded inside of the cylinder at a position 1½" from the bottom. A 1/8" air-purge pipe is located 1/2" from the bottom, where air is introduced at a flowrate of 228 ml/second.

Filter media core samples were taken from the HEPA filters with a hollow drill. The cores are 2¾" in diameter and 2½" in height. The filter media core is carefully inserted inside the reaction vessel, sitting on the fixed screen. A movable screen is then put on top of the filter media core to hold it from moving upward during the reaction.

Both the bottom and the top of the reaction vessel are closed with plastic lids. On the top lid, there are two openings; the large one in the center is to accept a condenser, and the small one by the side is for a thermometer probe. The reaction vessel is put in a water bath with constant temperature control.

During the test, one filter media core with 6 grams of calcine particles was put inside of the reaction vessel, which had been filled with 400-ml 2N nitric solution at a specified temperature. After reaction at the specified temperature for a specified period of time, the calcine residue were separated from the filter media and dried in an oven at 60ºC over

night. The calcine residue was weighed and the dissolution percentage was calculated from the weights of calcine feed and residue.

RESULTS AND DISCUSSIONS

Reproducibility

Four tests were first performed under exactly the same conditions (nitric acid concentration = 2 N, temperature = 88ºC, and reaction time = 0.5 hour) to assess the reproducibility of the experimental system. The results are given in Table I, where SD represents the standard deviation, and RSD represents the relative standard deviation.

The results indicate that the reproducibility of the experiment system is very good. Under the above conditions, the dissolution percentages of aluminum calcine and zirconium calcine are 78.6±3.1% and 97.8±0.6%, respectively.

Table I. The Calcine Dissolution Percentages and Statistics of the Reproducibility Tests (Nitric Acid = 2 N, T = 88ºC, Reaction Time = 0.5 hr)

Calcine	Calcine Dissolution, %				Statistics, %		
	1	2	3	4	Average	SD	RSD
Al	76.2	82.1	77.5	79.2	78.6	3.1	3.9
Zr	97.1	98.3	98.0	97.4	97.8	0.6	0.6

Nitric Acid Addition Orders

Two acid addition orders were designed. The first one called "bulk addition", in which the nitric acid solution is added in one shot. The second one called "incremental addition", in which nitric acid is added in 3 steps. For the incremental addition, two sets of tests were performed (see Table II). In both sets of tests, the total nitric acid additions are 2N (1N + 0.75N + 0.25N). The difference between the two sets is the reaction time. For set A, the total reaction time is 1 hour (0.5 hour + 0.25 hour + 0.25 hour). For set B, the total reaction time is 2 hour (1.0 hour + 0.5 hour + 0.5 hour).

Under temperature of 88ºC, experiments of nitric acid addition order were conducted for both aluminum and zirconium calcines. The results are shown in Table III and Figure 1. It is apparent that for zirconium calcine, the dissolution percentages achieved by incremental addition and bulk addition are almost the same. For aluminum calcine, the dissolution percentages achieved by incremental addition are even 8-9% lower than those achieved by bulk addition. It is concluded that the incremental addition does not improve the calcine dissolution.

Reaction Temperatures

With nitric acid concentration of 2 N and reaction time of 1 hour, a series of experiments were conducted to study the effect of the reaction temperature. The temperatures used are 30ºC (room temperature), 45ºC, 60ºC, 75ºC, 88ºC, and 99ºC (boiling point). The results are given in Table IV and Figure 2. It apparent that heating is critical in achieving high calcine dissolution. Below 60ºC, calcine dissolution percentages increase rapidly with temperature. When temperature rises from 30ºC to 60ºC, the dissolution percentages rise from 12% to 77% for aluminum calcine and from 46% to 91% for zirconium calcine.

Table II. Scheme of the Acid Dosage and Time Intervals for the Incremental Addition Tests

Test Set	**Nitric Acid Addition, N**			**Time Intervals, hour**		
	1	**2**	**3**	**1**	**2**	**3**
A (1 hr)	1.0	0.75	0.25	0.5	0.25	0.25
B (2 hr)				1.0	0.5	0.5

Table III. Comparison of the Calcine Dissolution Percentages Achieved by Nitric Acid Bulk Addition and Incremental Addition (Nitric Acid = 2 N, T = 88ºC)

Additional Order	Calcine Dissolution, %			
	Al/1 hour	Zr/1 Hour	Al/2 Hour	Zr/2 Hour
Bulk	64.7	84.9	76.8	83.7
Incremental	57.2	85.9	67.9	83.1

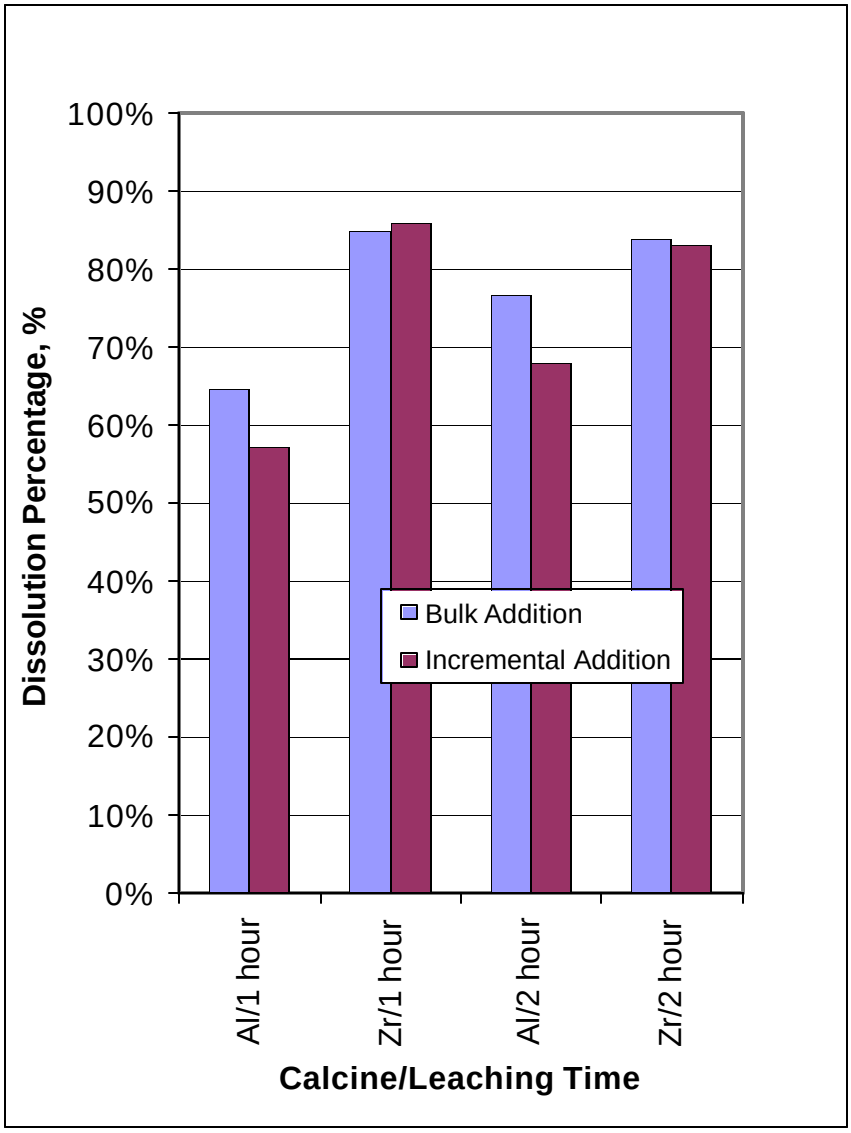

Table IV. Dissolution of Calcine (wt%) Under Various Temperatures (Nitric Acid = 2 N, Reaction Time = 1 Hour)

Calcines	Temperatures, °C					
	30	**45**	**60**	**75**	**88**	**99**
Aluminum	11.9	56.1	77.4	80.3	84.8	86.9
Zirconium	46.2	68.4	90.9	96.4	98.8	99.9

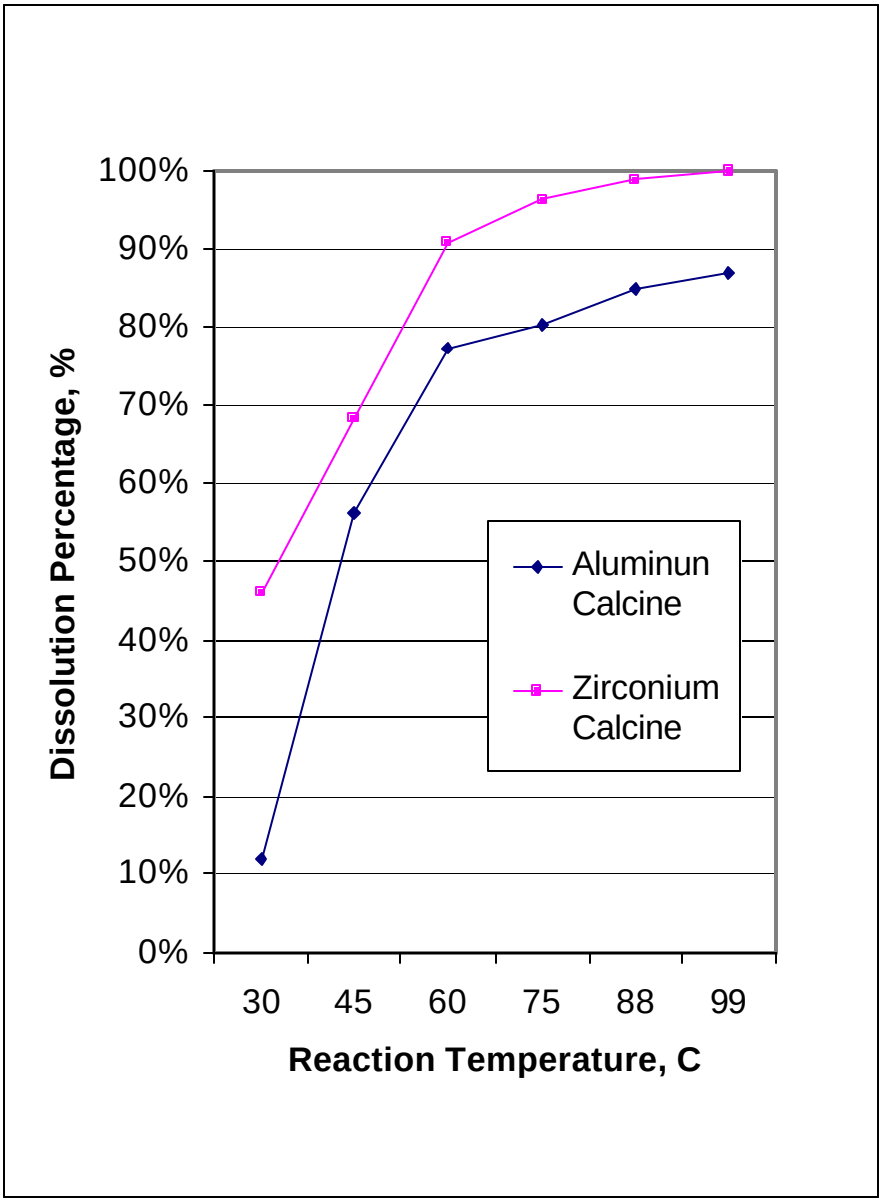

Figure 2. Dissolution of Calcine (wt%) Under Various Temperatures (Nitric Acid = 2 N, Reaction time = 1 Hour)

After 60ºC, the dissolution percentages still increase with the increase of the temperature but at much lower rates. When temperature rises from 60ºC to 99ºC, the dissolution percentages rise from 77% to 87% for aluminum calcine and from 91% to 100% for zirconium calcine.

Since temperature 88ºC is the one used by the current FLS and it's easy to reach and handle, it was the temperature adopted in the following comparison experiments.

Comparison of "Sandwich" Process and Pulp Process

Under the optimum conditions obtained from the prior experiments (nitric acid = 2 N, bulk addition, and temperature = 88ºC), tests were conducted to compare the "sandwich" and pulp processes. Four tests were performed at different reaction times: 0.5 hour, 1.0 hour, 2.0 hours and 4.0 hours. The results of aluminum calcine are given in Table V and Figure 3. The results of zirconium calcine are given in Table VI and Figure 4. It apparent that under the same conditions, calcine dissolution percentages achieved in pulp process are significantly higher than those achieved in the "sandwich" process. For example, with a reaction time of 0.5 hour (the reaction time used in current FLS), the pulp process increased the dissolution percentages by 19% and 17% for aluminum calcine and zirconium calcine, respectively.

These results are very encouraging and promising in demonstrating the advantages of the pulp process over the current process.

PLAN FOR FUTURE EXPERIMENTS

A complete evaluation of the pulp process will require more work to be done in the following areas:

1. When the experiments of this study were designed, we assumed that all the contaminants in the HEPA filter are contained in the calcine particles alone. But the real situation may be different. The hazardous metals and radioactive elements could also be adsorbed in the filter media. Therefore, in order to obtain more conclusive results we need to use the HEPA filter media contaminated with Cd, Cr, Hg and some other hazardous metals through a similar process as those HEPA filers do from the real operation. For easy handling, the media is to be non-radioactive. In these tests, the concentration of one or all elements will be used as criteria to judge the efficiency of the leaching process.

2. Besides chemical dissolution, physical separation is another option to clean the HEPA filter media for Pulp Process. If a physical separation is feasible and applied, the corrosive waste generation may be eliminated altogether. Therefore, laboratory tests are planned to develop a physical separation process. As a first step, the blend of shredded clean filter media and non-radioactive calcine particles will be used as the feed.

Table V. Dissolution of Aluminum Calcine (wt%) Obtained by "Sandwich" Tests and Pulp Processes (Nitric Acid = 2 N, T = 88ºC)

Processes	**Reaction Time, Hours**			
	0.5	**1.0**	**2.0**	**4.0**
Pulp	78.6	84.8	91.0	86.8
"Sandwich"	59.7	64.7	76.8	71.7

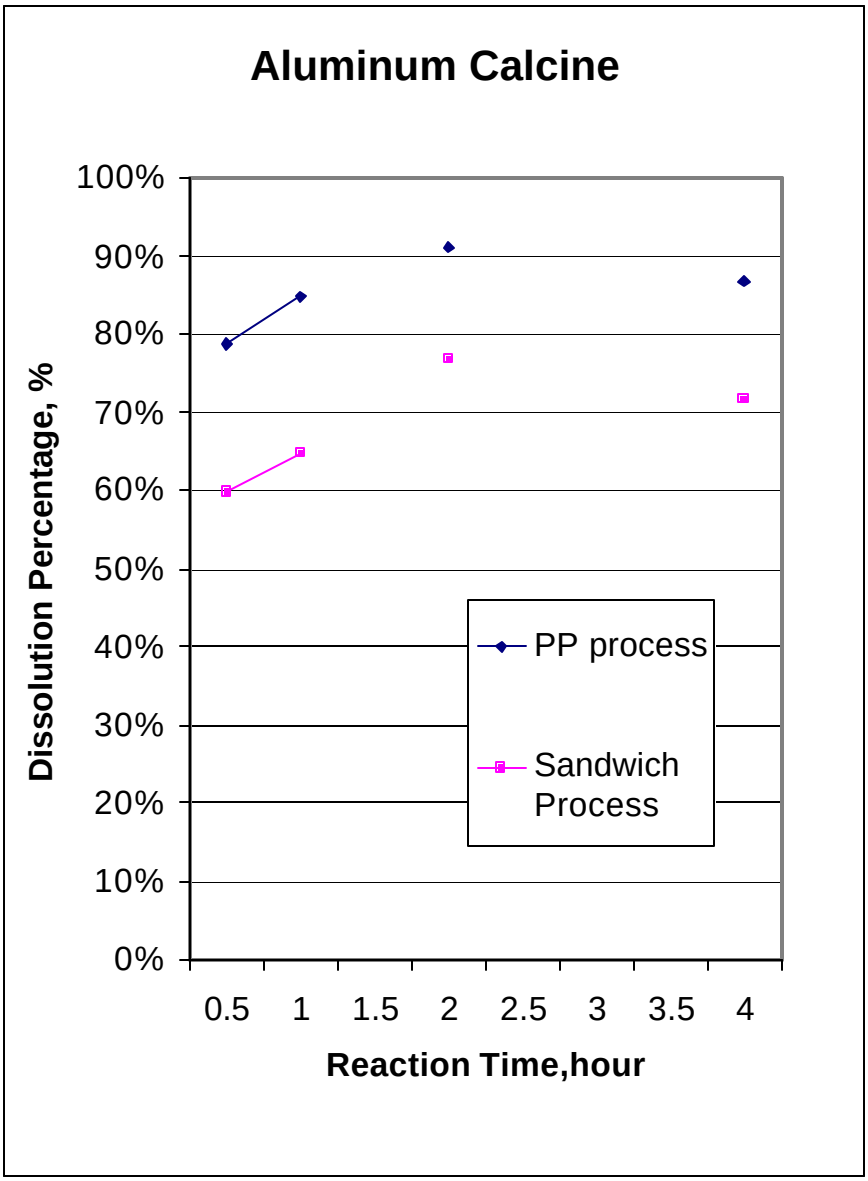

Figure 3. Dissolution of Aluminum Calcine (wt%) Obtained by "Sandwich" Tests and Pulp Processes (Nitric Acid = 2 N, T = 88ºC)

Table VI. Dissolution of Zirconium Calcine (wt%) Obtained by "Sandwich" Tests and Pulp Processes (Nitric Acid = 2 N, T = 88ºC)

Processes	**Reaction Time, Hours**			
	0.5	**1.0**	**2.0**	**4.0**
Pulp	97.8	98.8	99.3	99.0
"Sandwich"	80.5	84.9	83.7	90.1

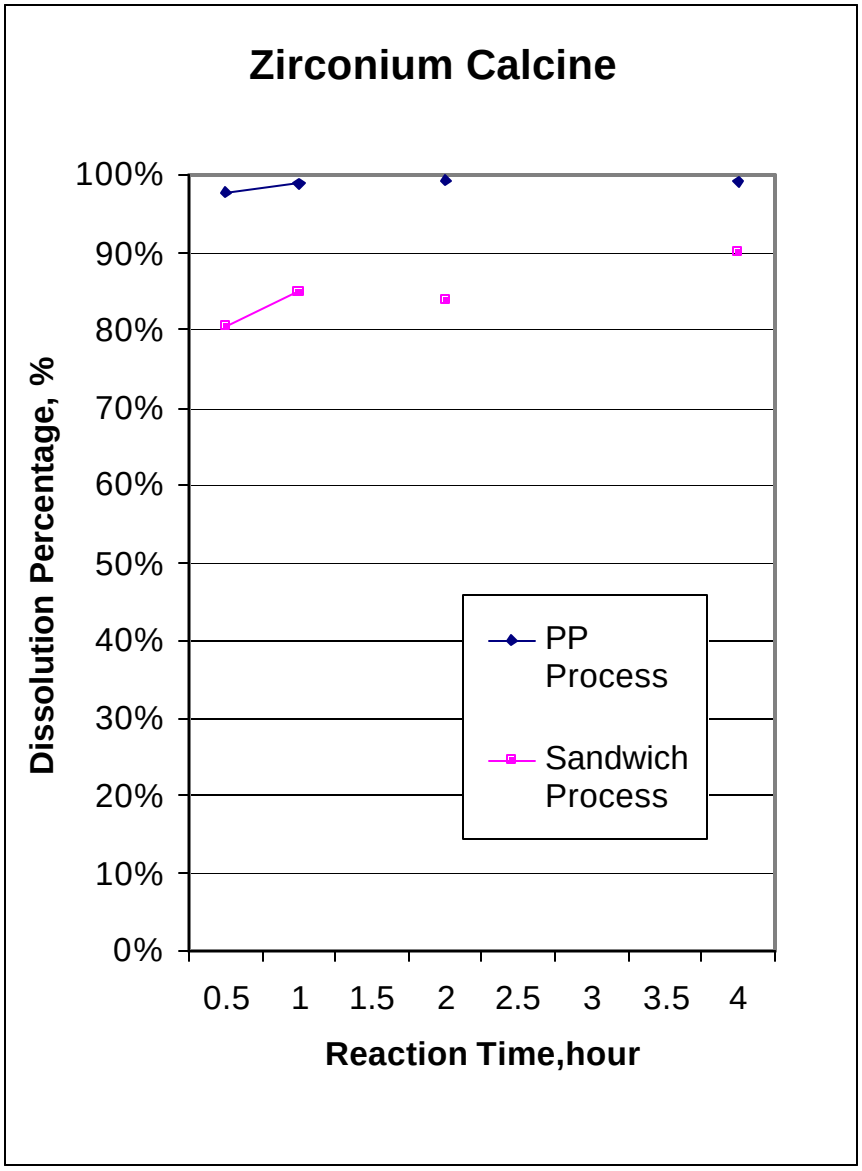

Figure 4. Dissolution of Zirconium Calcine (wt%) Obtained by "Sandwich" Tests and Pulp Processes (Nitric Acid = 2 N, T = 88ºC)

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