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DEVELOPMENT OF A PULP PROCESS TREATING CONTAMINATED HEPA FILTERS (PART I)

J. S. Hu, R. L. Demmer, and M. D. Argyle
Idaho National Engineering and Environmental Laboratory
P.O. Box 1625, Idaho Falls, ID 83415-5218

ABSTRACT

The current HEPA Filter Leaching System (FLS) at the Idaho National Engineering and Environmental Laboratory (INEEL) treats the whole filter unit with the filter media and trapped calcine particles being confined in the heavy filter housing. Low permeability, channeling, and dead zones around the edge of the housing contribute to poor mass transfer and inefficient liquid-solid separation during leaching and washing.

In order to improve the efficiency of the FLS, a Pulp Process has been proposed. In this process, the filter media and the trapped calcine particles are separated from the filter housing and treated as pulp. Chemical dissolution, physical separation or both can be used to separate calcine particles from the filter media in the Pulp Process.

A preliminary analysis showed that compared to the FLS, the Pulp Process could reduce the amount of corrosive liquid waste by a factor of 25 if chemical dissolution is applied. If a physical separation is feasible and applied, the corrosive waste generation may be eliminated altogether. Additionally, the Pulp Process can handle filters of different sizes and remove mercury more effectively.

This paper reports the results of the first phase of the laboratory experiments evaluating the Pulp Process. The objectives of this phase were to search for less corrosive dissolution reagents to replace nitric acid, to examine the operational conditions of the current FLS, and to establish the basis for physical separation. Six dissolution reagents (nitric acid, oxalic acid, sodium formate, Corpex 921, Turco 4502, and Turco ARR) were screened and two types of calcine (aluminum and zirconium) were tested.

The experimental results indicate that among the six dissolution reagents, nitric acid was the most effective. Aluminum calcine was less soluble than zirconium calcine in nitric acid and its highest solubility was only 56% under the applied conditions. Both calcines dissolved little in water, which met the prerequisite for a physical separation method.

More tests will be conducted in the second phase of the laboratory experiments: 1) Optimization tests to improve the calcine solubility. 2) "Sandwich tests" to demonstrate the advantages of the Pulp Process in comparison with the current FLS. 3) Characterization of the HEPA filters to determine the state and concentrations of the hazardous and radioactive metals. 4) Development of a filter dissembling technique to separate the filter media from the filter housing easily, safely, and economically. 5) Bench scale tests of the selected physical separation methods with simulated filter media samples.

INTRODUCTION

HEPA Filter Leaching

Operations at the Idaho National Engineering and Environmental Laboratory (INEEL) use high-efficiency particulate (HEPA) filters to prevent air pollution. As a result, many mixed waste HEPA filters have been generated. No favorable disposal options are currently available for the untreated HEPA filters as a result of their high level radioactive and hazardous contaminates.

The HEPA Filter Leaching System (FLS) located at Idaho Nuclear Engineering and Technology Center (INTEC) of the INEEL was built in 1988 (1,2), modified in 1992 (3) and validated in 1995 (4). It treated 78 filters in 1997 and 1998 (5). The FLS leaches the filters in nitric acid solution with concentrations of 1-2 M at a temperature of 88ºC for 30 minutes/cycle. It consists of 3 cycles of acid leaching and 2 cycles of water washing.

The FLS treats the filter housing and media together. Since the filter media and the trapped calcine particles are confined in a heavy filter housing, low permeability, channeling, and dead zones around the edge of the housing contribute to poor mass transfer and inefficient liquid-solid separation during leaching and washing. As a result, the FLS has the following shortcomings:

- Large volume of corrosive liquid waste generated – 300 gallons/filter
- Long cycle time – 18 hours/filter
- Ineffective mercury removal
- Lack of versatility in treating filters of various sizes

Pulp Process

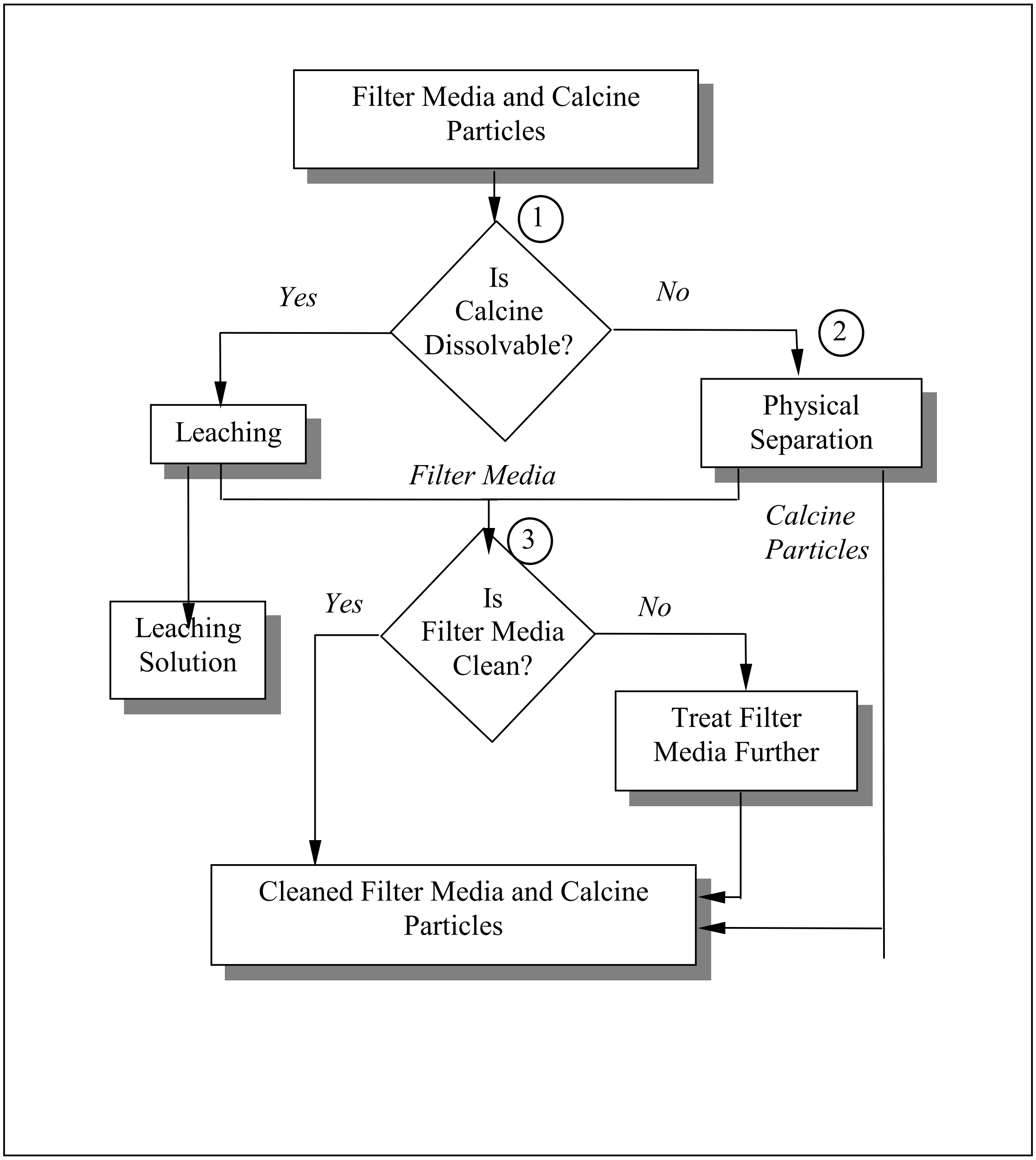
In order to improve the efficiency of the FLS, a Pulp Process has been proposed. In this process, the filter media and the trapped calcine particles are separated from the filter housing and treated as pulp. Chemical dissolution, physical separation, or both can be used to separate calcine particles from the filter media.

A preliminary analysis (6) indicated that filter media from ten filters could be treated in one batch of the Pulp Process. The leaching cycles could be reduced from 3 to 1, and the washing cycles from 2 to 1. Calculations based on these assumptions showed that, compared with the current FLS, the Pulp Process could reduce the amount of corrosive liquid waste by a factor of 25 and cycle time by a factor of 3 if the chemical dissolution is applied. If a physical separation is feasible, corrosive waste generation may be eliminated altogether. Additionally, the pulp process can handle filters of different sizes and remove mercury more effectively.

Rational of Method Selection

As shown in Figure 1, the selection of the cleaning methods for the Pulp Process is decided by three factors: 1) The solubility of calcine particles in the dissolution reagent. 2) The size distribution of the calcine particles trapped in the filter media. 3) The characterization of the radioactive and hazardous metals in the HEPA filters.

Figure 1. Rational of Method Selection in the Pulp Process



Scope

Overall, the HEPA filter cleaning problems can summed up as follows: 1) The current HEPA FLS needs improvement. 2) The pulp process is potentially superior to the current one. 3) The solubility of calcine is critical in determining what process can be adopted and how successful the process will be. Accordingly, the scope of this laboratory work is threefold: 1) search for less corrosive dissolution reagents to replace nitric acid, 2) examine the operational conditions of the current FLS, and 3) establish the basis for physical separations.

EXPERIMENT

Materials

Non-radioactive calcine from the pilot plant tests was collected in two portions: Bed and Fines. Fines were used in this experiment assuming that the calcine particles trapped in the HEPA filers are mostly fine particles.

The dissolution reagents included in this test were nitric acid, oxalic acid, sodium formate, and three commercial decontamination reagents, Corpex 921*, Turco 4502, and Turco ARR. The acids and salts were all of technical grade.

Solution Preparation

The standard concentration used in the screening tests was 2 M except that Oxalic acid and Turco 4502, which were limited by their saturation concentration at 1M. Since fresh Corpex 921 contains about 0.015M of its active component, it was used without dilution.

Apparatus

The laboratory setup included the following equipment:

- Four-neck Reaction flask (250 ml)
- Thermometer
- Air-sparging tube
- Condenser
- Heating mantle
- Electronic thermometer
- pH meter and probes
- Disposable filtering units (250 ml, pore size = 0.45 μm)
- Oven
- Balance

Experimental Conditions

The experimental conditions were as follows:

- Room temperature = 23ºC
- Elevated temperature = 88ºC
- Reaction time = 60 minutes

- Solid liquid ratio = 3.6 grams in 100 ml solution, and
- Sparging air flowrate = 450 ml/min.

Procedure

The experiments were conducted following the procedure below:

- Setup the reaction flask with the air sparging tube, the thermometer, and the condenser in three of its necks; place the flask on the heating mantle.
- Add 100-ml DI water into the reaction vessel through its 4th inlet, and turn on the sparging air at a flowrate of 450 ml/min. Turn on the heating mantle.
- Weigh and record 3.60 grams of calcine (Wo). When the temperature in the flask reaches the desired temperature add the sample into the reaction flask through the 4th inlet. Start the timer when the addition is done.
- Weigh and record the top part of the disposable filter with the filter paper in place (Wi), then reassemble the whole filter unit.
- Stop the sparging-air and pour the contents of the reaction flask into the filter unit when the reaction time reaches 60 minutes.
- Measure and record the pH of the filtrate collected in the bottom part of the filter.
- Drain the filter by gravity and then transfer the top part of the filter to the oven.
- Dry the top part of the filter in the oven at 60ºC over night.
- Weigh the top part of the filter and record its weight (Wf) after the filter unit is cooled down to the room temperature.
- Calculate and record the wt% dissolved utilizing the following equation:
  100 [(Wo + Wi) – Wf] / Wo %.

RESULTS AND DISCUSSIONS

Dissolution Reagents Screening

Aluminum Calcine. The solubilities of aluminum calcine in the six reagents are shown in Table I and Figure 2. Based on these results, the following conclusions can be drawn.

1. The dissolution powers of the reagents at elevated temperature, in the order of highest to lowest, were oxalic acid, nitric acid, Turco ARR, Turco 4502, Corpex 921, water, and sodium formate. The dissolving power of oxalic acid was equivalent, if not superior, to that of nitric acid.

2. The solubilities of aluminum calcine in sodium formate solution showed negative values, which was probably caused by precipitation.

3. Generally speaking, the calcine dissolved more at elevated temperature than at room temperature, and the reagent order of the solubility at room temperature was different from the order at the elevated temperature.

4. In water, aluminum calcines had low solubilities, 5.8% at elevated temperature and 9.56% at room temperature. It was intriguing that water dissolved more aluminum calcine at room temperature than at elevated temperature.

Zirconium Calcine. The solubilities of zirconium calcine in the six reagents are shown in Table II and Figure 3. Based on these results, the following conclusions can be drawn.

1. At elevated temperature, the dissolution powers of the reagents, in the order of highest to lowest, were nitric acid, Corpex 921, Turco ARR, Water, Turco 4502, sodium formate, and oxalic acid. It was obvious that nitric acid was much stronger than the rest of the reagents in dissolving zirconium calcine.

2. The solubilities of zirconium calcine not only showed negative values in sodium formate solutions but also in oxalic acid and Turco 4502 solutions. Again, this phenomenon was probably caused by precipitation.

3. The calcine was less soluble at room temperature than that at elevated temperature and the reagent order of the solubility at room temperature was different from the order at the elevated temperature.

4. In water, zirconium calcines had very low solubilities, 2.7% at the elevated temperature and 2.9% at room temperature. Temperature seemed to have no significant effect on the solubility of zirconium calcine in water.

Nitric Acid Concentration

Since nitric acid was the most effective dissolution reagent from the screening tests and the one used in the FLS as well, more tests were performed to study the effect of the nitric acid concentration.

Aluminum Calcine. The solubilities of aluminum calcine in various nitric acid concentrations are shown in Table III and Figure 4. Based on these results, the following conclusions can be drawn.

1. At elevated temperature, the solubility of aluminum calcine increased from 5.8% in water to 57.6% in 2-M nitric acid solution. However, the solubility leveled off at higher nitric acid concentrations. When the concentration of nitric acid increased from 2 M to 8 M, the solubility only slightly increased from 57.6% to 63.7%.

Table I. Solubilities of Aluminum Calcine (wt%) in the Screening Tests

Temp. ºC	Oxalic Acid	Nitric Acid	Turco ARR	Turco 4502	Corpex 921	Water	Sodium Formate
23	17.63	8.39	11.62	42.52	0.55	9.56	-10.82
88	58.46	57.56	50.97	39.28	15.37	5.82	-28.12

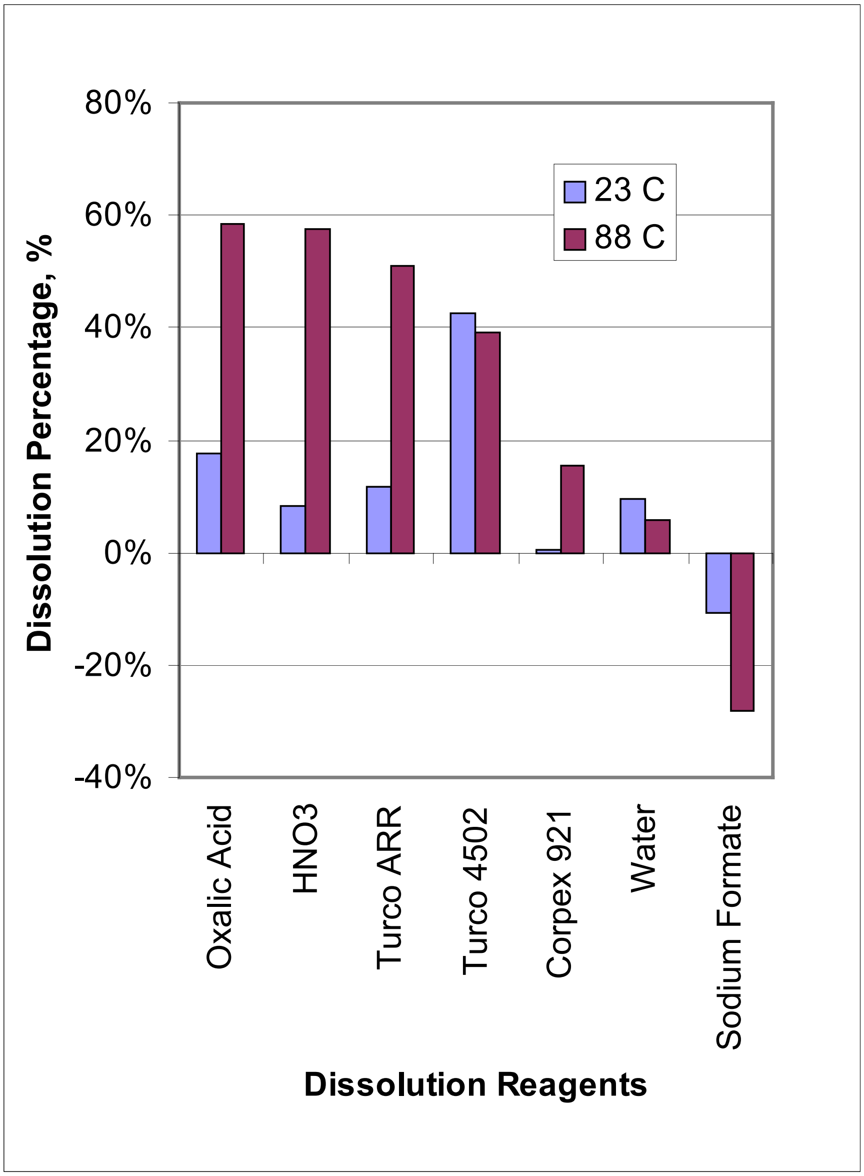


Figure 2. Solubilities of Aluminum Calcine (wt%) in the Screening Tests

Table II. Solubilities of Zirconium Calcine (wt%) in the Screening Tests

Temp. ºC	**Nitric Acid**	**Corpex 921**	**Turco ARR**	**Water**	**Turco 4502**	**Sodium Formate**	**Oxalic Acid**
23	58.97	-4.99	-0.69	2.90	-14.68	-10.82	-28.44
88	*87.60*	*21.21*	*13.30*	*2.70*	*-0.97*	*-17.22*	*-40.98*

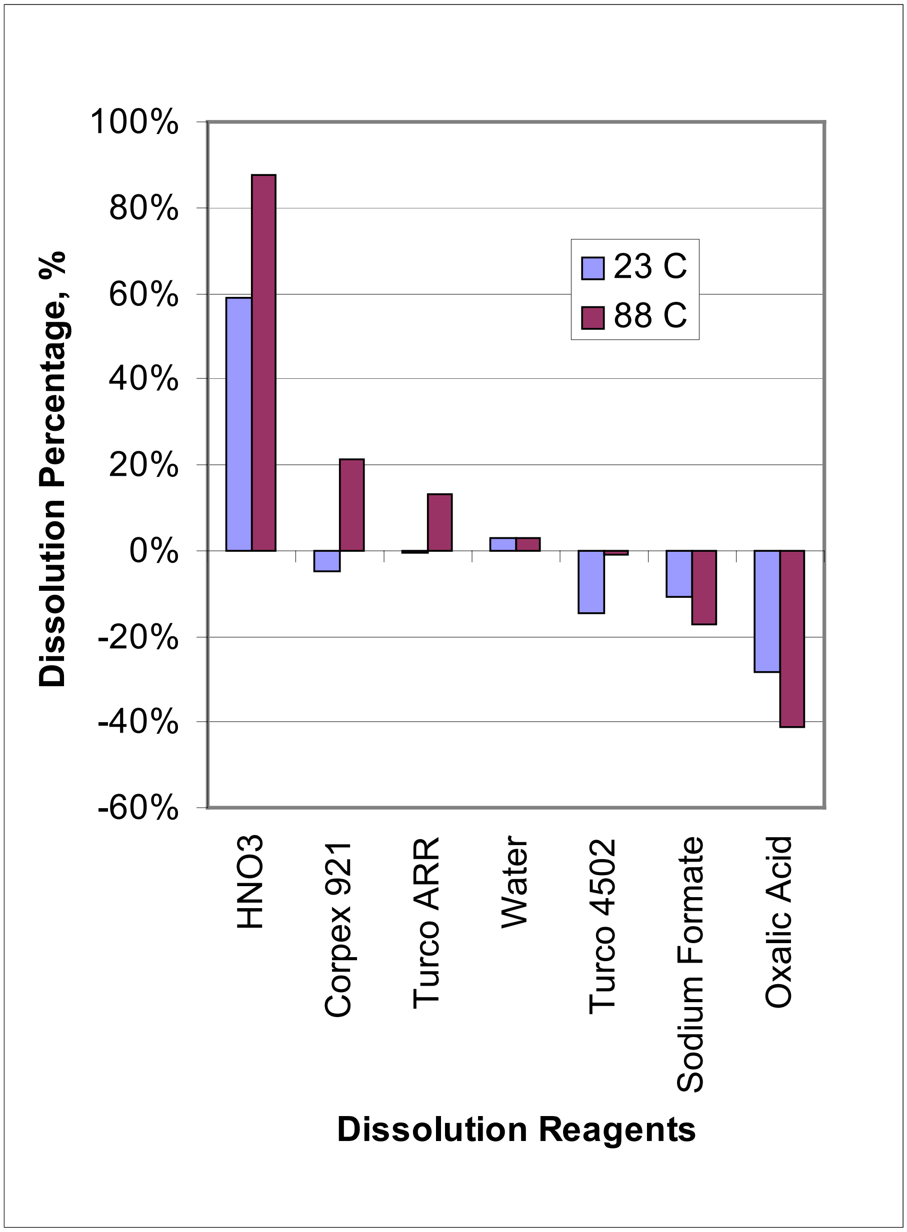


Figure 3. Solubilities of Zirconium Calcine (wt%) in the Screening Tests

2. At room temperature, the solubility of aluminum calcine was very low. Also, the solubility decreased as the concentration of nitric acid increased. This phenomenon indicated that more precipitates might form at higher nitric acid concentrations.

3. Aluminum calcine will not dissolve in nitric acid solution without heating; an increase of nitric acid concentration beyond 2M will not increase the calcine dissolution significantly; and nitric acid will not dissolve the calcine completely under the applied conditions.

Zirconium Calcine. The solubilities of zirconium calcine in various nitric acid concentrations are shown in Table IV and Figure 5. Based on these results, the following conclusions can be drawn.

1. At the elevated temperature, the solubility of zirconium calcine increased from 2.7% in water to 93.9% in 4-M nitric acid solution. However, the solubility leveled off at higher nitric acid concentrations. When the concentration of nitric acid increased from 4 M to 8 M, the solubility only slightly increased from 93.9% to 95.2%.

2. At room temperature the solubility of zirconium calcine increased from 2.9% in water to 71.5% in 4-M nitric acid solution. However, the solubility leveled off at higher nitric acid concentrations. When the concentration of nitric acid increased from 4 M to 8 M, the solubility actually dropped slightly from 71.5% to 69.7%.
3. Zirconium calcine will almost completely dissolve in nitric acid solutions at elevated temperature. Increase of nitric acid concentration beyond 4M will not increase the calcine dissolution significantly.

Synergistic Effect Studies

Previous results indicated that both nitric acid and oxalic acid can moderately dissolve aluminum calcine (at the elevated temperature, the solubilities of aluminum calcine in 2M nitric acid and 1M oxalic acid were 57.56% and 58.46%, respectively). If nitric acid is mixed with oxalic acid, will the mixture be a better dissolution reagent? In other words, is there any synergistic effect between nitric acid and oxalic acid?

To answer this question, tests using a mixture of 2M nitric acid and 1M oxalic were conducted. The results are given in Table V. At room temperature, the solubility of aluminum calcine in the mixture was 10.28%, which was slightly higher than the solubility in nitric acid (8.39%), but much lower than that in oxalic acid (17.63%). At the elevated temperature, the solubility of aluminum calcine in the mixture was 62.50%, which was only slightly higher than those in the individual acids (57.56% and 58.46%). Therefore no synergistic effect between nitric acid and oxalic acid was observed.

Table III. Solubilities of Aluminum Calcine (wt%) in Nitric Acid Solutions

Temp. °C	**Nitric Acid Concentration, M**				
	0	**2**	**4**	**6**	**8**
23	9.56	8.39	1.79	-5.82	-19.88
88	*5.82*	*57.56*	*56.17*	*61.55*	*63.66*

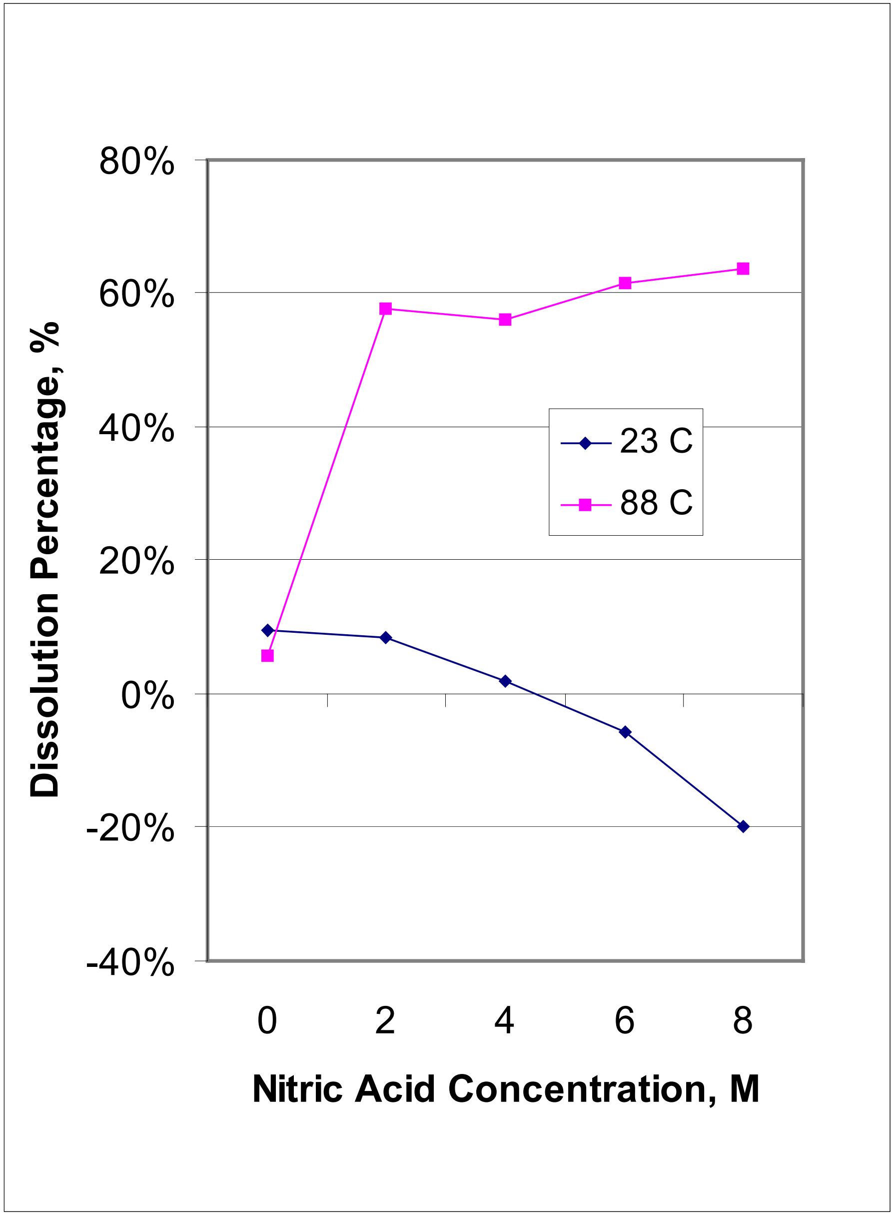


Figure 4. Solubilities of Aluminum Calcine (wt%) in Nitric Acid Solutions

Table IV. Solubilities of Zirconium Calcine (wt%) in Nitric Acid Solutions

Temp. ºC	**Nitric Acid Concentration, M**				
	0	**2**	**4**	**6**	**8**
23	2.90	58.97	71.47	67.55	69.67
88	*2.70*	*87.60*	*93.89*	*93.62*	*95.15*

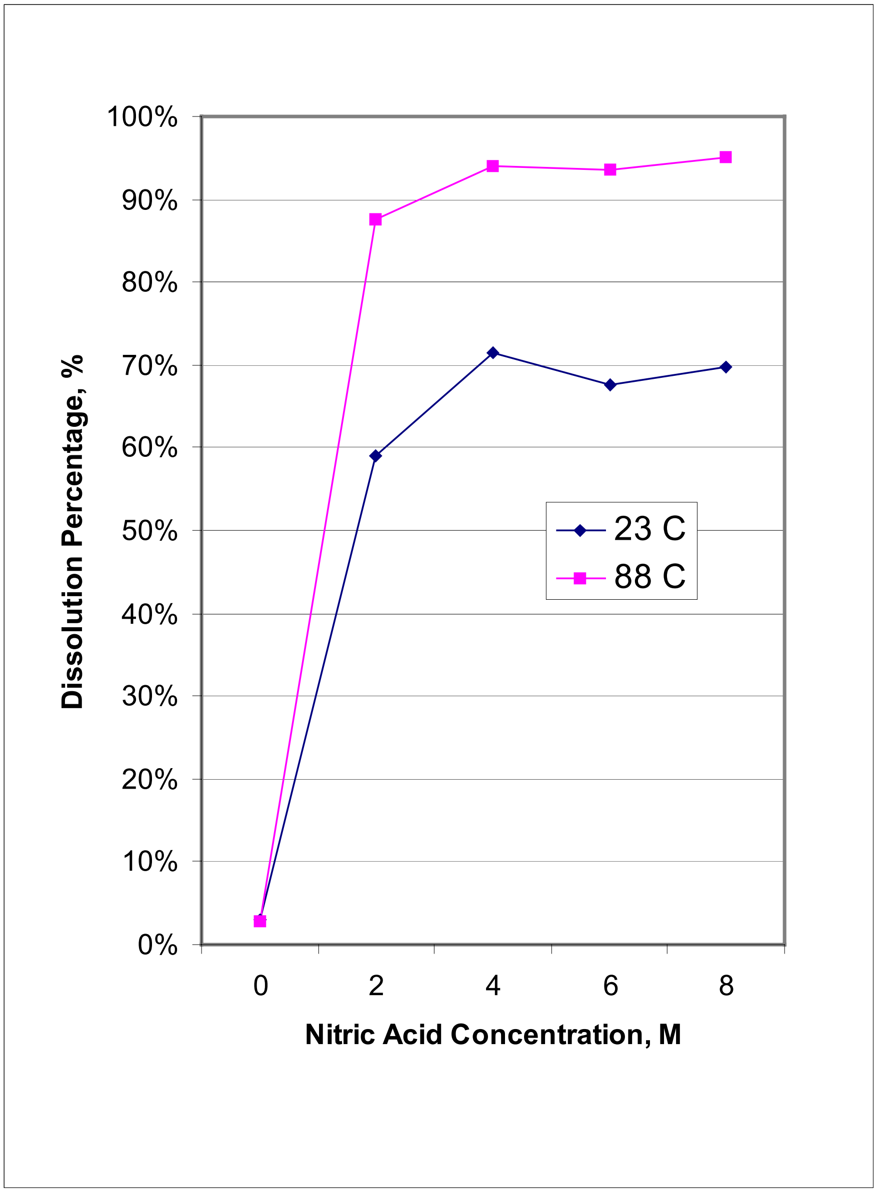


Figure 5. Solubilities of Zirconium Calcine (wt%) in Nitric Acid Solutions

Filtrate Recycling

From the previous tests, it was found that both aluminum and zirconium calcines were slightly soluble in water at room temperature (9.56% for aluminum calcine and 2.90% for zirconium calcine). This finding made the proposed physical separation technique, which requires the calcine particles to be insoluble in water, very promising.

In a physical separation process, water would be recycled. An experiment was conducted to study the change of the calcine solubilities in the filtrate-recycle process. In this experiment, a fresh calcine sample was first dissolved in fresh water to measure its solubility. Using the filtrate from this test, another fresh calcine sample was then dissolved into it, and its solubility was measured. This procedure was repeated 5 times, and the results are given in Table VI.

After only 2 recycles, zirconium calcine basically did not dissolve any more in the water. The solubility of aluminum calcine also steadily decreased with each recycle, dropping from 10.11% to 6.80% after 4 recycles.

Calcine Size Analyses

Previous results demonstrated that physical separations might be promising methods to treat the HEPA filters in the Pulp Process. For physical separation, the size distribution of the feed is important in feasibility-study, method-selection, and condition-determination. The size distributions of the two calcine samples were hence measured with an LS Particle Size Analyzer. The comparison of some key sizes of the two distributions is given in Table VII.

As you can see, their d_{50} (the size of which 50% of the particles are smaller than) were basically the same (aluminum calcine was 14.66 μm, zirconium calcine was 14.17 μm.). However, the d_{90} (the size of which 90% of the particles are smaller than) of aluminum calcine and zirconium calcine were 66.36 μm and 39.99 μm, respectively. This result indicated that aluminum calcine had more coarse particles.

Table V. Solubilities of Aluminum Calcine (wt%) in Nitric Acid Solution, Oxalic Acid Solution, and a Mixture of Both

Temperature °C	2M Nitric Acid	1M Oxalic Acid	2M Nitric Acid + 1M Oxalic Acid
23	8.39	17.63	10.28
88	57.56	58.46	62.50

Table VI. Calcine Solubilities (wt%) Affected by the Number of Filtrate Recycling

Calcine	**Number of Recycle**				
	0	**1**	**2**	**3**	**4**
Al	10.11	8.31	8.02	7.91	6.80
Zr	3.87	1.39	0.55	-1.25	-0.69

Table VII. Some Key Numbers of the Calcine Size Distributions

	d_{10}	d_{25}	d_{50}	d_{75}	d_{90}
Aluminum Calcine, µm	2.674	6.316	14.66	34.93	66.36
Zirconium Calcine, µm	3.166	7.097	14.17	24.43	39.99

	-200 mesh	**-400 mesh**
Aluminum Calcine	92%	77%
Zirconium Calcine	97%	89%

Converting to mesh size, -200 mesh of aluminum calcine and zirconium calcine was 92% and 97%, respectively. –400 mesh of aluminum calcine and zirconium calcine was 77% and 89%, respectively. Materials in this size range will be a challenge for physical separation techniques. Because of agglomeration, however, the sizes of the particles trapped in the HEPA filter are expected to be coarser. If so, a few physical separation methods, such as screening, flotation, shaking table, and fine-particle hydrocyclone would be feasible.

SUMMARY AND FOLLOW-UP WORK

Summary

1. Among the 6 reagents screened, nitric acid and oxalic acid were the best dissolution reagents for aluminum calcine, and nitric acid was the best for zirconium calcine. The mixture of nitric acid and oxalic acid did not improve the dissolution of aluminum calcine. Therefore, the search for a replacement of the current dissolution reagent, nitric acid, was not successful.

2. The most effective nitric acid concentration was 2M for both calcines. Heating was necessary to reach high solubilities.

3. At elevated temperature, 93.9% of zirconium calcine but only 56.2% of aluminum calcine will be dissolved by nitric acid.

4. Both aluminum calcine and zirconium calcine showed low solubilities in water at room temperature. This met the pre-requisite of physical separations.

5. The solubilities of aluminum calcine and zirconium calcine decreased as the dissolution solution was recycled.

6. The size distributions of both calcines (77% -400 mesh for aluminum calcine fine and 89% -400 mesh for zirconium calcine fine) will challenge the physical separation techniques. Because of agglomeration, however, the sizes of the particles trapped in the HEPA filters are expected to be coarser. If so, a few physical separation methods, such as flotation, screening, fine-particle hydrocyclone, and shaking table could be feasible.

Further Work

The work presented in this report is the results of the first phase of the laboratory experiments. To follow up, five more tasks as listed below need to be accomplished in the next phase of the laboratory experiments.

1. Optimization of the Chemical Dissolution Process
   More extensive experiments should be conducted to improve the calcine dissolution in nitric acid solutions. For example, stronger agitation (overhead mechanic agitation instead of air sparging), boiling-temperature, and successive addition of nitric acid need to be evaluated.

2. Sandwich Tests
   Based on the preliminary analysis, the Pulp Process will significantly reduce the waste volume and cycle time by improving the mass transfer and solid/liquid separation. To confirm this analysis, a sandwich test is to be conducted to compare the Pulp Process to the FLS. In this test, the solubility of calcine particles suspended in filter media pulp will be compared with the solubility of the same calcine particles sandwiched in layers of filter media under the same operation conditions.

3. Characterization of the HEPA Filters
   The hazardous and radioactive metals in the HEPA filers need to be characterized to address the following unknowns:
   - Whether the hazardous and radioactive metals only exist in the calcine particles, or also absorb on the filter media?
   - Which forms and concentrations do the metals exist? For example, does mercury exists as oxide, nitrate, chloride, elemental, or as all four?
   - What is the size distribution of the calcine particles?

   Because of the highly radioactive nature of the HEPA filters, collection of the above information will be challenging. Nonetheless, it will be necessary to work closely with the Analytical Laboratory, the Filter Leaching System personnel, and the HEPA filter generators to gather as much data as possible.

4. Filter Dissembling Method Development
   Whether chemical dissolution or physical separation will be eventually chosen for the Pulp Process, the filter media needs to be separated from its housing. An easy, safe, and economical dissembling method must be developed.

5. Bench Tests of Physical Separation Methods
   If it is determined that a physical separation is preferred to the chemical dissolution, the chosen physical separation methods must be tested in the laboratory with simulated samples.

FOOTNOTES

[*] Mention of specific products and/or manufacturers herein implies neither endorsement or preference, nor disapproval by the U. S. Government, any of its agencies, or Bechtel BWXT Idaho, LLC. of the use of a specific product for any purpose.

REFERENCES

1. R. I. Donovan, B. H. O'Brien, Letter to G. W. Hogg, "NWCF HEPA Filter Leaching Demonstration Results", July 31, 1984.

2. H. W. Thornton, "Design and Installation of a Radioactive Filter Leaching System at the Idaho Chemical Processing Plant", Proceedings, 36th Conference on Remote System Technology, 1988, Volume 2.

3. C. W. McCray, and K. N. Brewer, "HEPA filter Leach system Technical Basis Report", WINCO-1096, May 1992.

4. A. C. Chakravartty, "HEPA filter Leaching Concept Validation Trials at the Idaho Chemical Processing Plant", INEL-95/0182, April 1995.

5. Mark Argyle and Rick Demmer, "Development of a HEPA Filter Leach System", The 7th International Conference Proceedings on Radioactive Waste Management and Environment Remediation (ICEM'99), Nagoya, Japan, September 26-30, 1999.

6. Jian S. Hu, "Pulp Process – an Alternative Method for HEPA Filters Leaching", Presented in the Meeting of INTEC Corrosives Study, March 17, 1999.

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