144
5/20/69

799
IN-1276
April 1969

unclass
fc 5/22/69

MASTER

CLARIFICATION OF ELECTROLYTIC DISSOLVER
SOLUTION USING A HYDROCYCLONE

IDAHO NUCLEAR CORPORATION
NATIONAL REACTOR TESTING STATION
IDAHO FALLS, IDAHO

P1356

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

U. S. ATOMIC ENERGY COMMISSION

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

Printed in the United States of America
Available from
Clearinghouse for Federal Scientific and Technical Information
National Bureau of Standards, U. S. Department of Commerce
Springfield, Virginia 22151
Price: Printed Copy \$3.00; Microfiche \$0.65

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, express or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

IN-1276

Issued: April 1969

Chemical Separations Processes
for Plutonium and Uranium

TID-4500

CLARIFICATION OF ELECTROLYTIC DISSOLVER SOLUTION USING A HYDROCYCLONE

by

D. H. Cranney*
M. E. Jacobson
B. C. Musgrave

*Summer employee during 1968 in Idaho Nuclear Corporation's cooperative program with university science and engineering departments. Present address: Brigham Young University, Provo, Utah.

IDAHO NUCLEAR CORPORATION

A JOINTLY OWNED SUBSIDIARY OF
AEROJET ALLIED
GENERAL CHEMICAL
CORPORATION CORPORATION

U. S. Atomic Energy Commission Research and Development Report
Issued Under Contract AT(10-1)-1230
Idaho Operations Office

REPRODUCTION OF THIS DOCUMENT IS UNLIMITED

leg

A B S T R A C T

Four laboratory-scale hydrocyclones were evaluated for their efficiency in clarification of product solution from electrolytic dissolution of EBR-II fuel. Ninety-five percent removal of stainless steel solids from the overflow stream was demonstrated at 45 psi pressure drop through a hydrocyclone which was 38 mm in diameter and 264 mm long. At these same conditions, ten percent removal of EBR-II fissium alloy residues was attained.

S U M M A R Y

Solid materials as undissolved remnants and insoluble products result from the electrolytic dissolutions of nuclear reactor fuels. Diversion of these solids from the recycle stream of the electrolytic dissolver, with ultimate removal by a centrifuge, will help to reduce fouling of process equipment.

Several hydrocyclones were evaluated for their potential usefulness in clarification of plant process streams. Particular emphasis was placed on the behavior of the solids resulting from dissolutions of stainless steel and EBR-II fuel in the electrolytic dissolver. At the approximate pressure drops that would be practical for a plant installation, 95 percent of the smaller sized stainless steel solids were removed by the hydrocyclone; at these same conditions, only 10 percent of the fissium alloy residues from EBR-II fuel were removed. Interactions between large amounts of solids and high concentrations of silica gel were also examined. None of the mixtures tested, short of a firm gel, caused any decrease in the effectiveness of the hydrocyclone for particle separation.

C O N T E N T S

	page
ABSTRACT	ii
SUMMARY	iii
I. INTRODUCTION	1
II. OPERATIONAL CHARACTERISTICS OF THE HYDROCYCLONE	4
III. EXPERIMENTAL SECTION	6
1. SOLID PARTICLES	6
2. PROCEDURE	6
IV. RESULTS	7
1. STAINLESS STEEL PARTICLES	7
2. ADDED MATERIAL	7
2.1 Gases	7
2.2 Silica Gel	7
2.3 Firm Gel	10
2.4 Fissium Solids	10
2.5 High Solids Concentration	11
3. DISTRIBUTION OF PARTICLE SIZES	11
V. RECOMMENDATIONS AND APPLICATIONS	13
IV. REFERENCES	14 /

F I G U R E S

	page
1. Conceptual design of electrolytic dissolution system showing possible use of hydrocyclone to control solids	2
2. Typical hydrocyclone	4
3. Characteristic efficiency curve for a hydrocyclone	5
4. Effect of pressure drop on separation of solids	8
5. Photographs of particles removed in the underflow during Run 2	12

T A B L E S

1. Separations Attained with Laboratory Hydrocyclones	9
---	---

CLARIFICATION OF ELECTROLYTIC DISSOLVER SOLUTION USING A HYDROCYCLONE

I. INTRODUCTION

As part of a program of investigation of the problem of handling and disposition of the solids from electrolytic dissolution of stainless steel-clad fuels, the evaluation of various hydrocyclones for possible use in solids diversion was undertaken.

The solids which must be handled include (1) partially dissolved grains or clusters of grains from the metal, (2) insoluble products such as hydrated oxides resulting from dissolution of fuel components, and (3) insoluble fractions of the fuel meat or cladding. These may be accompanied by polymerized silica resulting from the dissolution of the silicon which is always present in the alloys at least as a trace impurity.

Grains which fall undissolved from the stainless steel matrix during electrolytic dissolution continue to dissolve as long as they remain suspended in the electric field⁽¹⁾; however, once these particles are removed from the active area of the dissolver, dissolution ceases and the problem of their removal arises. The fuel alloy from EBR-II is uranium - 5 percent fissium. The fissium alloy is 50 percent molybdenum and 40 percent ruthenium; the remainder of this part of the fuel alloy consists of minor amounts of zirconium, palladium, and niobium. Some of these materials will dissolve chemically or electrochemically in the electrolytic dissolver. Insoluble oxides will form in some cases; ruthenium forms a series of complex compounds based on the $\text{Ru}(\text{NO})(\text{III})$ core; some of these are also insoluble.

Various amounts of other insoluble materials may result from components of the fuel mixture or cladding alloy. Zirconium, when present, is converted electrolytically in nitric acid to the insoluble oxide⁽²⁾. Some other alloying elements can be expected to behave in a similar manner. If not removed from the stream, these particles deposit throughout the recycle system. Association of this material with silica gel forms a sludge which can reduce the effectiveness of the system in the critical matters of heat transfer and electrolysis current. Silicic acid which has been produced in the dissolution of the fuel components rapidly polymerizes to silica gel in high-salt-content acid media⁽³⁾.

The very small size of many of these particles makes their removal in settling tanks impractical. Since the product stream will be clarified continuously by passage through a centrifuge, a reduction of this sludge problem in the recycle stream would be obtained by concentrating the bulk of the solids into the product withdrawal stream by means of a hydrocyclone.

A possible installation of a hydrocyclone in the electrolytic dissolution system is shown in Figure 1. Here, the product from the dissolver is fed to the hydrocyclone while a maximum amount of the solids are still suspended in the solution; solids in the underflow stream would be removed in the continuous centrifuge. The overflow of the hydrocyclone to the recycle stream would be clarified sufficiently to significantly reduce the problem of sludge formation and solids deposition⁽³⁾.

Figure 1 Conceptual design of electrolytic dissolution system showing possible use of hydrocyclone to control solids.

A common application of the hydrocyclones is solid-liquid separations where the density ratios are in the range of 2 to 3. Stainless steel particles have a density of at least 5 times that of the dissolver product solution; this factor aids in the separation of the fine particles and will enhance the separation at the low underflow fraction required for the electrolytic dissolver installation. Hydrocyclones are frequently used with an underflow 25-40 percent of the throughput⁽⁴⁾; for the electrolytic system, the recirculation rate required for temperature control will limit the withdrawal rate to the range of 2 to 10 percent of the throughput. This low underflow rate puts some limitation on the clarification which can be achieved by a hydrocyclone.

Because of these uncertainties in the possible efficiency of a hydrocyclone in this application, laboratory tests were initiated on

a series of glass units. Measurements of hydrocyclone efficiency were made with stainless steel grains alone over the range of most of the variables studies. Later measurements evaluated the effects of fissium solids and of silica gel.

II. OPERATIONAL CHARACTERISTICS OF THE HYDROCYCLONE

A sketch of a hydrocyclone is shown in Figure 2. The solid-liquid mixture enters the inlet aperture under pressure; the underflow and overflow are generally operated at free discharge. The tangential entry directs the stream in a circular path; a flow pattern is established by the centrifugal force with liquid and solids moving out and downwards. The particles are separated from the liquid by this centrifugal action. At a point part way down the cone the liquid flow near the center reverses direction to pass upward and out through the overflow. The bulk of the solids are concentrated in the underflow stream. The performance of the cyclone depends on several factors, including size, shape, and density of the particles, density of the liquid, pressure drop between inlet and overflow, the ratio of underflow to overflow, the diameter and the angle of the conical section, and the diameter of the cylindrical section of the hydrocyclone. Since the factors relating to the particles and solution were fixed by the nature of the electrolytic dissolver product, only the effect of pressure drop and hydrocyclone design were evaluated for this mixture.

Fig. 2 Typical hydrocyclone.

For any application of a hydrocyclone for clarification of a stream, the fraction of the total solids removed will be characteristic of the given particle size distribution; almost complete removal of solids above a certain size will be expected for a particular hydrocyclone at a given set of operating conditions⁽⁴⁾; likewise, for some minimum size the separation efficiency will be nil. For a distribution of sizes of solids of one density then, varying efficiencies with size will be expected. The separations achieved at a given pressure drop are schematically illustrated in Figure 3.

At a given set of operating conditions the particle size scale to be fitted to the curve in Figure 3 is dependent on the density ratio between the solid and liquid phases. The minimum percent separation illustrated here is simply the percent of the solution which is cut to underflow when no enhancement is seen due to the hydrocyclone action. The maximum separation will be limited by short circuit flow at the top of the hydrocyclone.

Figure 3 Characteristic efficiency curve for a hydrocyclone

INC-A-13000

III. EXPERIMENTAL SECTION

1. SOLID PARTICLES

The stainless steel particles used in these experiments were recovered from sludge generated during operation of the electrolytic dissolver pilot plant⁽⁵⁾. To remove silica and soluble oxides these solids were washed alternately with 10 percent NaOH, water, 4M HNO₃, and water followed by centrifuging after each wash. The particles were recovered on a 5-micron filter. Examination of this solid material under the microscope revealed that most of the particles smaller than 5-micron were retained on the filter. Beginning with Run 4, the measurements were made using solids which passed through a 325 mesh (44 μ) sieve.

2. PROCEDURE

Most of the runs were made with 1.5 gm of solids in three liters of water. The screened solids were maintained suspended in the water in the reservoir by a mechanical stirrer. The mixture was pumped at the desired rate through the hydrocyclone; the underflow and overflow were collected in separate vessels. The pressure of the input solution was measured at the inlet to the hydrocyclone; the fraction split between overflow and underflow was controlled by a pinch clamp on the underflow. Both the overflow and the underflow were operated at free discharge (no hydrostatic back pressure). The overflow solution was then returned to the reservoir to be recycled through the hydrocyclone. The solids in the underflow stream were removed by filtration and weighed. Initially, these samples were collected on 5-micron filters which removed all but an insignificant amount of material; however, starting with Run 8, the solids were collected on a 1.2-micron filter.

The range of experiments was limited by the pressures and throughput capacities of the available pumps plus safety factor allowance for the glass. Most of the experiments were run at about 25 psig pressure drop.

The solution left in the reservoir was removed after each cycle so that the efficiency of the hydrocyclone could be determined for those solids which were actually passed through it. The residual solids left in the reservoir were also measured to verify that all of the initial solids were recovered.

In Run 16, cyclones 1 and 2 were stacked in series. The underflow from unit 1 was fed to the input of unit 2. The underflow from the first hydrocyclone was 50 percent. The second hydrocyclone was set at 20 percent underflow for a net 10 percent cut in two steps.

IV. RESULTS

1. STAINLESS STEEL PARTICLES

The separations achieved with the various hydrocyclones are summarized in Table I. The experimental conditions are listed along with the percent solids removed on each cycle. These results are also plotted in Figure 4 where the influence of pressure drop on separation efficiency is readily apparent. From Runs 4, 9, and 14 (Table I) it is apparent that the geometry of the hydrocyclone within this range of sizes did not make a major difference in the separations achieved. The separation achieved with each of these hydrocyclones shows approximately the same dependence on pressure drop. The stacked hydrocyclone experiment, Run 16, did not give satisfactory clarification because proper balance of the flow was not possible with the equipment being used.

The commercial unit, Number 5, was too large for high pressure tests to be run with laboratory equipment. Its relative effectiveness is indicated by the two experiments that were run at pressure drops of 10 and 18 psig.

2. ADDED MATERIALS: GASES, SILICA GEL AND HIGH SOLIDS

2.1 Gases

The product from the electrolytic dissolver is saturated with oxides of nitrogen. In order to evaluate the difficulties which might be caused by the bubbles formed by the oxides of nitrogen, a run was made with the solution saturated with N_2O . No significant difference in separation efficiency was observed in these experiments compared to experiments with solution free of such dissolved gases. Since the solution was saturated at one atmosphere external pressure before it entered the hydrocyclone, as the electrolytic stream will be, the considerably higher pressure in the hydrocyclone prevented significant bubble formation. The release of small amounts of additional gases in the vortex of the hydrocyclone should not seriously hamper its operation.

2.2 Dilute Silica Gels

Run 13 gives some indication of the behavior of stainless steel-silica gel sludge. The concentrations of the stainless steel solids and the silica were approximately those anticipated in the ICPP process electrolytic dissolution. The solution was prepared at the desired silica concentration with stainless steel solids present. At the time at which the gel formation became apparent, the reaction flask was swirled so that the metal solids became suspended in the silica gel. This mixture of the suspended solids in the dilute, flocculent gel was

Figure 4 Effect of pressure drop on separation of solids

TABLE 1

SEPARATIONS ATTAINED WITH LABORATORY HYDROCYCLONES

Except where specifically noted the feed solution contained 0.5 g of stainless steel particles per liter in water.

Run	Cyclone Number	Hydrocyclone Pressure	Overflow (liter/min)	Underflow (liter/min)	% Available Solids Removed Per Cycle				
		Drop (psi)			First	Second	Third	Fourth	Residue
1	2	4	3.2	0.30	59±5	13	8.3	3.9	9.7
2	2	10	5.9	0.55	69±5	16	5.5	2.3	---
3	2	21.5	8.6	0.92	80±5	14	4.1	1.5	1.9
4	2	23	8.9	1.0	90±2	7.1	1.2	0.5	0.7
5	3	10	6.3	0.57	77±5	13	3	1	---
6	3	13	7.5	0.15	85±2	7.4	2.1	1.2	3.8
7	3	13	7.5	0.75	88±2	5.4	1.7	0.6	1.3
8	3	21	8.9	0.80	78±5	13	2.5	0.4	---
9	3	22	9.6	0.86	86±2	8.9	1.4	0.5	0.6
10	3	25	10.9	0.22	91±2	4.1	1.4	0.6	1.7
11	3	45	14	0.30	95±2	---	---	---	---
12	1	26	8.9	0.18	88±2	6.1	1.4	0.8	2.2
13[a]	1	26	8.6	0.51	84±2	---	---	---	---
14	1	26	8.6	0.86	91±2	5.7	1.7	0.6	1.0
15	1	26	8.6	0.86	87±2	6.1	1.3	0.5	1.3
16	1,2	26/12	8.6	0.86	60±2	17.4	6.4	4.0	4.9
17	5	10	40	0.80	69±2	---	---	---	---
18	5	18	51	1.0	77±2	---	---	---	---
19[b]	3	25	11	1.1	47±5	13.2	6.6	---	---
20[b]	3	45	14	0.27	63±5	---	---	---	37
21[c]	3	45	13	0.13	9.2±2	8.6	4.4	---	---

[a] Contained silica gel at a level of 296 mg Si/l in 8M HNO₃

[b] Contained fissium and stainless steel solids in 8M HNO₃

[c] Contained fissium solids only in 7.6M HNO₃

Cyclone Designation (All dimensions are external)

1. 19 mm diameter - 200 mm length
2. 19 mm diameter - 230 mm length
3. 38 mm diameter - 265 mm length
4. 65 mm diameter - 300 mm length
5. Commercial Unit, 76 mm diameter - 840 mm length

pumped through the hydrocyclone system in the usual manner. As the sludge passed through the hydrocyclone, the stainless steel particles were separated as though the gel were not present.

The addition of silica gel at low concentration, as described for Run 13, caused no apparent inhibition of the action of the hydrocyclone. In Run 15, at an underflow of 10 percent of the throughput, a separation of 87 percent was achieved. In Run 13 at 6 percent underflow, the separation was 84 percent. This difference in separation is apparently due to the decreased fraction taken to the underflow and should not be attributed to significant effects due to the silica gel. Analysis of the silica concentration in the underflow fractions from Run 13 shows that no enhanced separation of the silica gel is achieved. This result is not unexpected due to the small difference in the densities of the silica gel and water.

Runs Number 9 and 11, Table I, further compare the effectiveness of pressure increase for enhanced separations. In hydrocyclone Number 3, the increase from 23 to 45 psi pressure drop increased the first cycle separation from 86 to 95 percent. This represents a decrease of about 65 percent in the amount of solids passed to the recirculation stream. Although further testing at higher pressures was considered to be unsafe in the glass equipment in use here, the upper pressure drop tested approaches that which is practical for an in-plant installation. Significant improvement would not be expected for markedly higher pressures. For this reason, the separation effected in an optimized plant installation should not greatly differ from these results. The remaining solids are made up primarily of the finer size ranges which will be very difficult to separate at any pressure drop⁽⁴⁾.

2.3 Firm Gel

A run, not reported in Table 1, was made with a silicon concentration of 1 gm per liter in 2.6M HNO₃. This concentration produced a firm gel⁽³⁾ which was broken sufficiently to permit pumping and then passed through the hydrocyclone. The presence in the mixture of globules of this rigid gel did not hamper the flow through the hydrocyclone. Solids suspended in a firm gel were not separated as cleanly as had been accomplished with the dilute or flocculent-type gel, Run 13.

2.4 Behavior of Fissium Solids

The separation of fissium solids was investigated in Runs 19-21. These experiments were carried out with the limited amount of solid materials available. The attainment of realistic operating conditions in this short time is perhaps open to question. Run 19 at 25 psi pressure drop and Run 20 at 45 psi pressure drop indicate that a significant enhancement of the separation occurs due to this increase of pressure drop. Run 21 at 45 psi pressure drop with fissium solids alone resulted in 9.2 percent removal in a 2 percent underflow.

2.5 High Solids Concentration

In a qualitative test, solutions containing about 10 grams of stainless steel particles per liter were pumped through the hydrocyclone. Separation was achieved without any indication of hampered flow. No indication of a tendency to clog the flow was observed at any time in this test.

3. DISTRIBUTION OF PARTICLE SIZES

The particles recovered from the various cycles through the hydrocyclone were examined microscopically. Photographs taken with a Polaroid camera through a Unitron model Bux-11 microscope were compared and counted using a calibrated overlay grid. The change in the distribution of sizes is quite apparent from comparison of the photographs in Figure 5; attempts at quantitative measurement of the actual sizes proved unsatisfactory. Accuracy of the measurement was limited by the non-uniformity of the slides being compared and by the uncertainty in the estimation of sizes.

Even without a quantitative count, the removal of the larger sized particles with successive cycles is clearly seen; for a given amount of material in the slide, a much smaller number of large particles is present from the fourth cycle. The complete removal of the large sized particles has not occurred before the fourth cut. This is consistent with the existence of short circuit paths for some of the solution through the hydrocyclone. Large particles can be carried through the unit without being subjected to the centrifugal forces for a sufficient period of time to cause their removal.

After first cycle

After second cycle

After third cycle

After fourth cycle

Figure 5 Photographs of particles removed in the underflow during Run 2. Magnification: 100 times.

V. CONCLUSIONS AND RECOMMENDED APPLICATIONS

From a limited number of experiments with three hydrocyclones, some indication of the potential utility of a hydrocyclone for clarification of an ICPP process stream has been obtained. The mixtures used here simulated the stream anticipated from the electrolytic dissolution of EBR-II fuel. The complex mixtures expected in this stream did not interact under any conditions to foul the hydrocyclone; only under the most adverse and scarcely credible conditions was the separating action of the hydrocyclone hampered.

In the first pass, diversion of 90 percent or greater of the stainless steel solids and approximately 10 percent of the fission solids from the overflow stream should be expected for the solids generated in the electrolytic dissolution of EBR-II fuel. In later passes the separation efficiency drops off sharply.

The installation of a hydrocyclone in the electrolytic process stream just downstream from the dissolver will be optimum for clarification of the recirculating stream. Solids freshly released from the fuel will be removed most effectively. The steady state recirculating stream in the dissolver system can be expected to remain at or below the instantaneous single cycle overflow concentration of solids from the hydrocyclone. Therefore, the stream flowing from the hydrocyclone to the heat exchanger and the rest of the recirculation loop will be carrying a maximum of 10 percent of the stainless steel grains that are dropped in the dissolver. The low efficiency attained for the fission solids clearly indicates that these materials will remain in the recirculating stream at a high steady state concentration to deposit at points throughout the system. The relatively small size of these particles will increase the probability that they will remain suspended and not settle out in any part of the system.

VI. REFERENCES

1. J. R. Bower, Ed., Chemical Processing Technology, Quarterly Progress Report, October-December 1963, IDO-14635, p. 16 (March 1964).
2. M. R. Bomar, Electrolytic Oxidation of Zirconium in Nitrate Solution, IDO-14571, (December 1961).
3. D. H. Cranney and B. C. Musgrave, Factors Influencing the Rate of Silica Gel Formation in High Acid-Salt Solutions, IN-1270, (February 1969).
4. D. Bradley, The Hydrocyclone, Pergammon Press, New York, 1965.
5. R. A. Brown, et al, A Pilot Plant Study of the Electrolytic Dissolution of Stainless Steel Fuels, IN-1196, (to be published).