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Development of Ultrafiltration and Inorganic Adsorbents for Reducing Volumes of Low-Level and Intermediate-Level Liquid Waste: April-June 1978

William R. Herald and Raymond C. Roberts

July 19, 1978

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Miamisburg, Ohio

operated by
MONSANTO RESEARCH CORPORATION
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U. S. DEPARTMENT OF ENERGY

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Foreword

Under the sponsorship of the DOE Division of Waste Management, Mound is responsible for the development and demonstration of separation methods for removing radionuclides from intermediate-level and low-level liquid processing wastes prior to introduction into a combined waste stream.

This report is submitted by W. T. Cave, Director, Nuclear Operations, and B. R. Kokenge, Manager, Nuclear Technology, from contributions prepared by members of the Nuclear Waste Technology Section, K. V. Gilbert, Manager, and the Volume Reduction Technology Group, W. H. Bond, Leader, under the technical guidance of J. W. Koenst.

Previous reports on this project are listed below:

Development of Ultrafiltration and Inorganic Adsorbents for Reducing Volumes of Low-Level and Intermediate-Level Liquid Waste:

April-June 1977	MLM-2464
July-September 1977	MLM-2499
October-December 1977	MLM-2503
January-March 1978	MLM-2513

Contents

Abstract

A series of runs was performed in which waste processing facility influent was spiked with americium-241, neptunium-237, and uranium-233 and run through the ultrafiltration and reverse osmosis (RO) units. The results of these experiments show that the ultrafiltration membranes are ionic dependent, whereas the RO unit is not. Membrane irradiation studies have been started. Continuous run parameters are being verified through a series of experiments.

The small laboratory column tests were continued this quarter on several adsorbents. Decontamination factors were calculated for these adsorbents in removing neptunium-237 and americium-241 from waste solutions. Tests were continued with the 2-in. Engineering Columns using ultrafiltration product spiked with uranium-233. A 6-in. diameter column was installed in the combined raffinate line from the three Engineering Columns. This "mixed bed" column will polish the waste solution that is returned to the waste processing facility tanks.

A quality control program was started this quarter.

Membrane pilot plant studies

Raymond C. Roberts

A series of runs was made in which the waste processing facility influent, used as feed, was spiked with americium-241, neptunium-237, and uranium-233. In each case, the pH of the influent was raised to 9.0 by the addition of NaOH, and a sample of the product after ultrafiltration was counted on a scintillation counter to determine the level of activity. After this, a known amount of the desired isotope (americium-241, neptunium-237, and uranium-233) was added, mixed, and run through the system. A sample was taken and counted on the scintillation counter to determine the total alpha level of the product. A sample of the product was then submitted for an alpha pulse height analysis to determine the isotopic makeup of the product.

During each run, 15 liters of product were collected and used as feed for the laboratory-scale reverse osmosis (RO) unit. Samples of the product from the RO runs were collected and analyzed to determine the total level of alpha contamination. Total rejection of activity for the two-stage treatment (UF and RO) was then calculated for each isotope.

The results of these runs showed that in the UF process, 98.9% of the plutonium-238 and americium-241 was rejected by the D membrane and 98.8% by the M. membrane. (The feed contained 280.2 dis/min/ml alpha whereas the product contained 2.9 dis/min/ml after the D membrane and 3.4 dis/min/ml after the M membrane.) An alpha pulse height analysis of this product showed that ∿66% of the activity in the product was from americium-241 and 34% from plutonium-238. The UF run made using plutonium-238 and neptunium-237, however, showed a rejection of activity of only 69.1% by the D and 70.9% by the M membranes. (The feed contained 130.6 dis/min/ml and the products contained 42.0 dis/min/ml after the D membrane and 38.0 dis/min/ml after the M membrane.) An alpha pulse height analysis of the product showed that 90% of the activity was from neptunium-237 and 10% from plutonium-238. Two runs were made using uranium-233 and plutonium-238 in the feed. In the first of these runs, rejection of activity was 83.7% by the D membrane and 84.6% by the M membrane. (Feed was 119.5 dis/min/ml and the products were 19.5 dis/min/ml after the D membrane and 18.4 dis/min/ml after the M membrane.) In the second run, rejections of activity were 98.6% by the D membrane and 98.4% by the M membrane. (The feed contained 331.0 dis/min/ml and the product contained 4.48 dis/min/ml after the D membrane and 4.23 dis/min/ml after the M membrane.) An alpha pulse height analysis of the product showed that the contamination was ∿50% uranium-233 and 50% plutonium-238.

Although the rejection of activity varied considerably from one ultrafiltration run to the next, after the 15-liter samples of product from each UF run were put through the RO unit, the total rejections of activity from two-stage runs (UF and RO) were very similar. The total rejection of americiaum-241 and plutonium-238 was 99.99% (final product, 0.3 dis/min/ml), of neptunium-237 and plutonium-238 was 100%, and of uranium-237 and plutonium-238 was 99.7% (final product, 0.4 dis/min/ml).

The conclusion drawn from the results of these experiments is that the ability of the UF membranes to reject a certain isotope is dependent upon how ionic the isotope remains at the pH at which it is processed. (Neptunium-237 is more ionic at pH 9 than uranium-233 which is more ionic at pH 9 than americium-241 or plutonium-238.) The more ionic it tends to remain, the less it will be removed by a UF membrane. The rejection of activity by the RO membrane, however, appears to be totally unaffected by the ionic makeup of the feed. A tabulation of the results of these runs can be seen in Table 1.

After the spiking runs were completed, the system was flushed with water to remove as much of the spiking isotopes (Am, Np, U) as possible, and a series of batch concentration runs were started. During the course of the first of these runs, 2,175 gal were processed to a final volume of 75 gal for a volume reduction of ∿29:1. The rejections of activity varied throughout the course of the run, but this is from normal changes in the makeup of the feed. The flux, however, remained very constant (∿2.0 gal/min at the beginning to 1.7 gal/min at the end). Suspended solids increased from ∿50 mg/liter at the start to ∿500 mg/liter at the finish.

During the course of the second run, 2,725 gal of feed were concentrated to ∿225 gal for a volume reduction of ∿12:1. The run had to be terminated at this point because of flux decline (flux went from ∿2.0 gal/min at the beginning to <0.75 gal/min at the end). Suspended solids increased from <50 mg/liter to ∿250 mg/liter at the end. A third run was begun, but it had to be

Table 1 - RESULTS OF UF AND RO RUNS MADE ON FEED SPIKED WITH AMERICIUM-241, NEPTUNIUM-237 AND URANIUM-233

Run No.	Volume of Feed (gal)	Alpha Activity of Feed Before Spiking (dis/min/ml)	Alpha Activity of Products Before Spiking (dis/min/ml)		Isotope Added (& Concentration)	Alpha Activity of Feed After Spiking (dis/min/ml)	Alpha Activity of Product After Spiking (dis/min/ml) and Amount Rejected (%)		Alpha Activity of Product After RO Run (dis/min/ml) and Amount Rejected (%)
			D	M			D	M	
1	300	260.4	4.0	4.1	Am^{241} ($46.5 x 10^6$ dis/min)	280.2	2.9 (98.9)	3.4 (98.9)	0.03 (99.99)
2	300	72.7	0.93	1.95	Np^{237} ($80 x 10^6$ dis/min)	130.6	42.0 (69.1)	38.0 (79.9)	0 (100)
3	450	101.2	1.6	1.7	U^{233} ($52 x 10^6$ dis/min)	119.5	19.5 (93.7)	18.4 (84.6)	0.4 (99.7)
4	200	271.8	6.21	4.72	U^{233} ($30 x 10^6$ dis/min)	331.0	4.48 (98.6)	5.27 (98.4)	--

terminated because of low flux. At this point, the system was shut down for a thorough cleaning. After the cleaning, a new run will be begun in which a concentration of 200:1 will be attempted.

Absorbent tests

W. R. Herald

Prefiltration effects on plutonium-contaminated wastes

At the startup of the Engineering Column test system, waste solution from the waste processing facility storage tanks was filtered through 100-μm filters and pumped to the column feed tank. The filtered solution was spiked with plutonium (IV) and sampled for alpha activity. This feed solution was then filtered through a 10-μm filter and sampled before being pumped to the feed inlets on the three Engineering Columns. The results of the 10-μm filtration are given in Table 2.

Decontamination factors (DFs) of 3.36 to 304.11 were calculated for the overall filtration. Generally higher alpha concentrations in the feed yielded greater DFs. This could be caused by a combination of several mechanisms: adsorption on <100-μm solids, polymerization of plutonium into large colloidal molecules, and adsorption on algae and bacteriological growth. No pattern was observed but tests proved that waste solutions with a pH range of 6 to 8 can be filtered to remove most of their plutonium activity. For example, a high-activity (3×10^{11} dis/min/ml), caustic (pH 8) plutonium-238 solution was filtered through a 100-μm and then a 1-μm filter. The filtrate from this system had an alpha concentration of 6.9×10^{6} for a calculated DF of 4.3×10^{4}.

Because of the problems associated with the anomalous results of the plutonium experiments, ultrafiltration product is now used in all tests. The product from the ultrafiltration system contains no suspended solids but has all the ionic species found

Table 2 - THE EFFECT OF FILTRATION ON PLUTONIUM-238 IN WASTE WATER WITH 10-μm FILTERS

pH	Feed Before Filter (dis/min/ml)	Feed After Filter (dis/min/ml)	DF
6	12,904	1,129	11.43
	8,118	1,150	7.06
	9,655	1,338	7.22
	9,493	1,302	7.29
	8,648	1,591	5.44
	20,220	425	47.58
	13,145	45	292.11
7	12,652	3,763	3.36
	19,767	65	304.11
	14,900	1,325	11.25
	13,145	89	147.70
8	25,874	1,214	21.31
	10,780	793	13.59
	14,900	767	19.43
	15,066	1,427	10.56

in waste streams. Another advantage is the rejection of alpha activity by ultrafiltration membranes (98% to 99.9%). With an initial alpha concentration of <5 dis/min/ml, it is easier to determine the removal of a specific spiked radioisotope from waste solution.

Laboratory columns

The small (7-mm diameter) laboratory column tests were continued during the quarter. These small column tests are being used to screen adsorbents for further testing on the 2-in. diameter Engineering Columns. The adsorption of americium-241 from waste solutions at pH 7 and pH 3 was tested. The results of these small column tests are given in Tables 3 and 4.

The best adsorbents tested at pH 7 were: HCR (DF 3.51), XE279 (DF 3.4), IRA-938 (DF 3.26), bone char (DF 2.7), D1X4 (DF 2.26), and WGR (DF 2.14). These adsorbers are anionic type, with the strong-base ones being better than the weak-base ones.

Greater decontamination factors (DF) were calculated when the hydrogen ion concentration was lowered to pH 3. The cationic type of resin becomes more effective because of the formation of more cations in solution. Bone char had the greatest DF (1568.0) at pH 3. In previous bone char experiments, it was observed that the bone char began dissolution at pH 4. The exact adsorption mechanism that occurred with the bone char at pH 3 is not well understood at this time. Several adsorbents gave excellent DFs of 10 or greater. Generally, a resin's adsorption ability is directly related to the solution's acidity.

The small (7-mm diameter) laboratory column tests with neptunium-237 are summarized in Table 5. Notable results were obtained with bone char (DF 33.77). All other adsorbents tested at pH 3 had a DF of 10 less than bone char. Resins AG1X4 (DF 3.46), MSA-1 (DF 2.76), MSC-1 (DF 2.79), SAR (DF 2.21), IRA-904 (DF 2.05), and 200 (DF 2.62) give fair neptunium removal from slightly acidic solutions. These resins are anionic type except for MSC-1 and 200 which are macroporous cationic resins.

Raffinate polishing column

A 6-in. diameter column was installed in the same fume hoods as the three Engineering columns (see Quality Control Flowsheet). The feed to the 6-in. column is the combined raffinate stream from the three 2-in. columns. This large 6-in. column is filled with a "mixed bed" of adsorbents to give a total bed height of 40.5 cm. The adsorbents are layered in the following order from the bottom to the top of the column.

Adsorbent	Dry Weight (g)	Height (cm)
MSC-1	708.5	7.6
Bone char	392.5	2.5
MSA-1	622.0	5.1
Bone char	409.5	2.5
XN1010	571.0	7.6
Bone char	1305.0	11.4
D 1X4	702.0	3.8

This "mixed bed" column will reduce the amount of radioisotopes transferred to WD waste process tanks. An average DF of 165 was achieved in removing uranium-233 from raffinates of the Engineering columns.

Quality control

A quality control program for the DWM-funded development project, "Development of

Table 3 - RESULTS FROM THE LABORATORY COLUMN TESTS WITH AMERICIUM-241

	Feed			Resin		
pH	Activity (dis/min/ml)	Flow Rate (ml/min)	Raffinate Activity (dis/min/ml)	Type	Height (cm)	DF
7	14430	2	7096	Bone char	7	2.03
7	14430	2	8107	XE270	7	1.78
7	14430	2	7861	WGR	7	1.84
7	14430	2	12682	AG50WX8	7	1.14
7	14430	2	9654	XE236	7	1.49
7	14430	2	8774	MWA-1	7	1.64
7	14430	2	6218	XE243	7	2.32
7	14430	2	13046	HCR	7	1.11
7	14430	2	6380	D1X4	7	2.26
7	14430	2	8492	IRA-430	7	1.70
7	14430	2	7243	IRA-900	7	1.94
7	14430	2	4422	IRA-938	7	3.26
7	14430	2	7220	MSC-1	7	2.00
7	14430	2	10820	XN1010	7	1.33
7	14430	2	6480	IRA-904	7	2.23
7	14430	2	9888	SAR	7	1.46
7	14430	2	4250	XE279	7	3.40
7	14430	2.3	6342	11	7	2.28
7	14430	2.3	5348	Bone char	7	2.70
7	14430	2.3	8218	XE270	7	1.76
7	14430	2.3	6734	WGR	7	2.14
7	14430	2.3	3512	AG50WX8	7	4.11
7	14430	2.3	11526	XE236	7	1.25
7	14430	2.3	8916	MWA-1	7	1.62
7	14430	2.3	7442	XE243	7	1.94
7	14430	2.3	4112	HCR	7	3.51
7	14430	2.3	7056	P1X4	7	2.05
7	21952	2.3	14602	IRC-50	7	1.50
7	21952	2.3	716	XN1010	7	30.66
7	21952	2.3	1260	200	7	17.42
7	21952	2.3	14223	IRA-904	7	1.54
7	21952	2.3	1213	MSC-1	7	18.10
7	21952	2.3	15244	MSA-1	7	1.44
7	21952	2.3	1348	AG1X4	7	16.28
7	21952	2.3	1587	AG1X4	7	13.83
7	21952	2.3	1329	D1X4	7	16.52
7	21952	2.3	14	Bone char	7	1568.00
7	21952	2.3	17439	IRA-938	7	1.26
7	21952	2.3	18182	IRA-430	7	1.21
7	21952	2.3	21081	SBR-P	7	1.40
7	21952	2.3	19697	11	7	1.11
7	21952	2.3	21234	XAD-7	7	1.03
7	21952	2.3	18312	IRA-900	7	1.20
7	21952	2.3	5651	XE236	7	3.88
7	21952	2.3	968	XE243	7	22.68
7	21952	2.3	17957	SAR	7	1.22
7	21952	2.3	206	XE270	7	106.56
7	21952	2.3	625	MWA-1	7	35.12
7	21952	2.3	866	HCR	7	25.35
7	21952	2.3	481	WGR	7	45.64
7	21952	2.3	451	AG-50W-X8	7	48.67

Table 4 - LABORATORY COLUMN ADSORBENTS RESIN STUDY WITH AMERICIUM-241: EFFECT OF pH

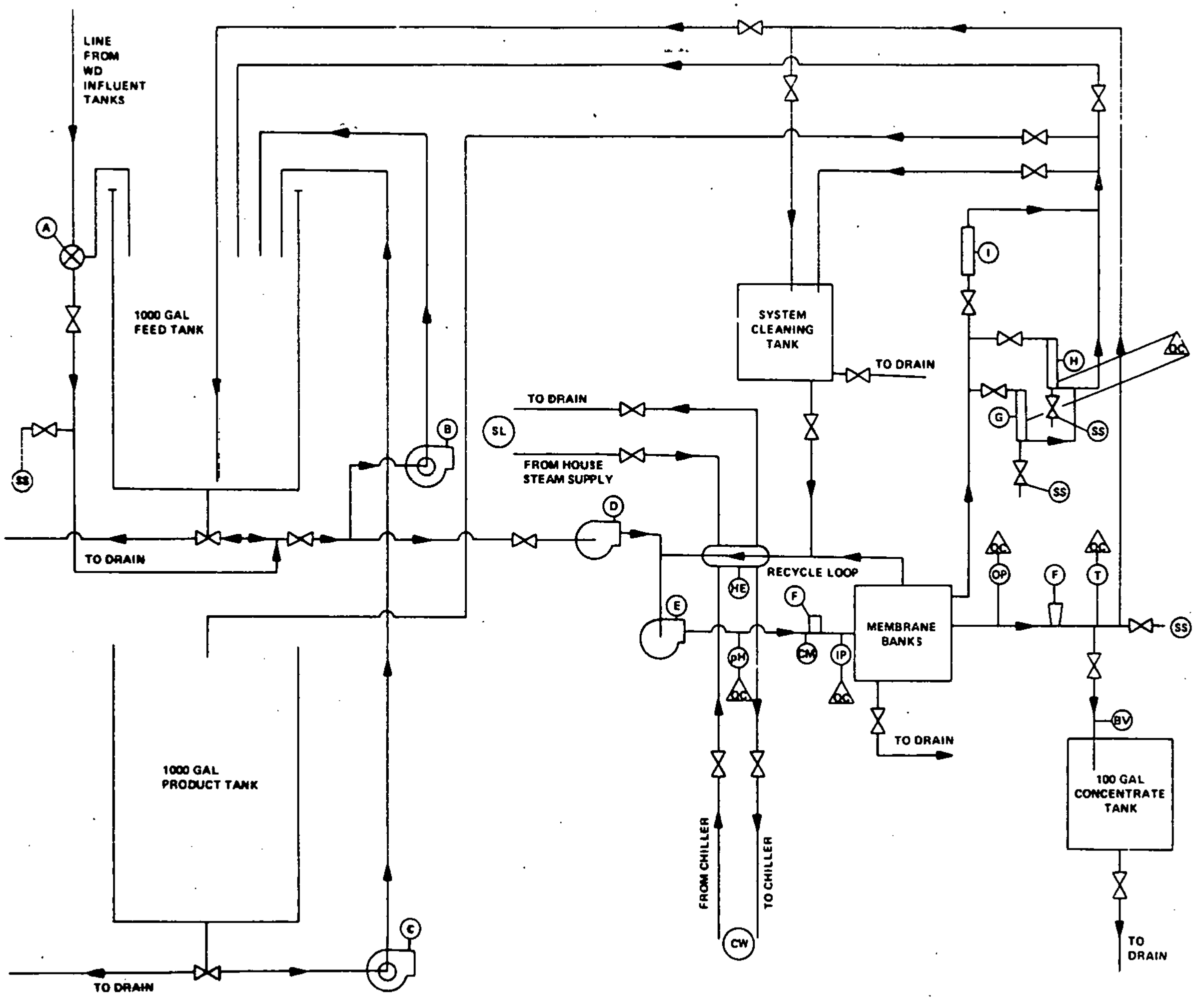
	pH 3			pH 7		
	Activity (dis/min/ml)			Activity (dis/min/ml)		
Resin	Initial	Raffinate	DF	Initial	Raffinate	DF
IRA-900	5100	2708	1.88			
IRA-430	5100	2559	1.99			
SAR	5100	2311	2.21			
11	5100	2565	1.99			
IRA-938	5100	2332	2.19	4132	970	4.26
XE279	5100	3210	1.59			
IRA-904	5100	2484	2.05			
MSC-1	5100	2428	2.10	4132	2224	1.86
XN1010	5100	2584	1.97	4132	2963	1.39
AG1X4	5100	1451	3.51	4132	2965	1.39
MSA-1	5100	1688	3.02	4132	2017	2.05
IRC-50	5100	3300	1.55	4132	2381	1.74
200	5100	1812	2.81	4132	2847	1.45
Bone char	5100	158	32.23	4132	1374	3.01

Table 5 - DECONTAMINATION FACTORS OBTAINED FROM THE LABORATORY COLUMN TESTS WITH NEPTUNIUM-237

	Feed		Raffinate	Resin		
pH	Activity (dis/min/ml)	Flow Rate (ml/min)	Activity (dis/min/ml)	Type	Height (cm)	DF
3	5100	2	2708	IRA-900	7	1.88
3	5100	2	2559	IRA-430	7	1.99
3	5100	2	2311	SAR	7	2.21
3	5100	2	2565	11	7	1.99
3	5100	2	2332	IRA-938	7	2.19
3	5100	2	3210	XE279	7	1.59
3	5100	2	2484	IRA-904	7	2.05
3	5100	2	2428	MSC-1	7	2.10
3	5100	2	2584	XN1010	7	1.97
3	5100	2	151	Bone char	7	33.77
3	5100	2	1944	200	7	2.62
3	5100	2	3404	IRC-50	7	1.50
3	5100	2	1829	MSC-1	7	2.79
3	5100	2	1849	MSA-1	7	2.76
3	5100	2	1472	AG1X4	7	3.46

Ultrafiltration and Inorganic Adsorbents for Volume Reduction of Liquid Waste," was started this quarter. The objective of this program is to generate reliable, traceable data. Because the developed technology is to be used in a full-scale operating system, the data must be valid. The quality control program is built upon process flow diagrams which identify the specific control mechanisms used to validate the data generated. These diagrams provide an easy way to check our quality control program during its development and to implement a more specific quality control program. A quality control organization is presently operational at Mound, but it has not previously scrutinized research and development projects.

The flow diagrams shown in Figures 1 and 2 identify the areas where quality control methods are used in the new procedures for both ultrafiltration and inorganic adsorbents programs.



LEGEND:

- (A) AUTOMATIC SHUT OFF VALVE TO PREVENT OVERFLOW
- (B) MIX PUMP
- (C) PUMP BACK TO FEED TANK
- (D) U.F. SYSTEM FEED PUMP
- (E) U.F. SYSTEM RECYCLE PUMP
- (F) GATE VALVES FOR CONTROLLING RECIRULATION AND FEED RATES
- (G) FLOW METER FOR D MEMBRANES
- (H) FLOW METER FOR M MEMBRANES
- (I) FLOW METER FOR COMBINED STREAM
- (T) TEMPERATURE SENSOR
- (pH) pH PROBE
- (BV) AUTOMATIC CONCENTRATE BLEED VALVE
- (CM) CONDUCTIVITY PROBE
- (IP) INLET PRESSURE GAGE
- (OP) OUTLET PRESSURE GAGE
- (SS) SAMPLE STATION
- (HE) HEAT EXCHANGER
- (CW) CHILL WATER LINES TO & FROM HEAT EXCHANGER
- (SL) STEAM LINES TO & FROM HEAT EXCHANGER

FIGURE 1 - Ultrafiltration process flow diagram.

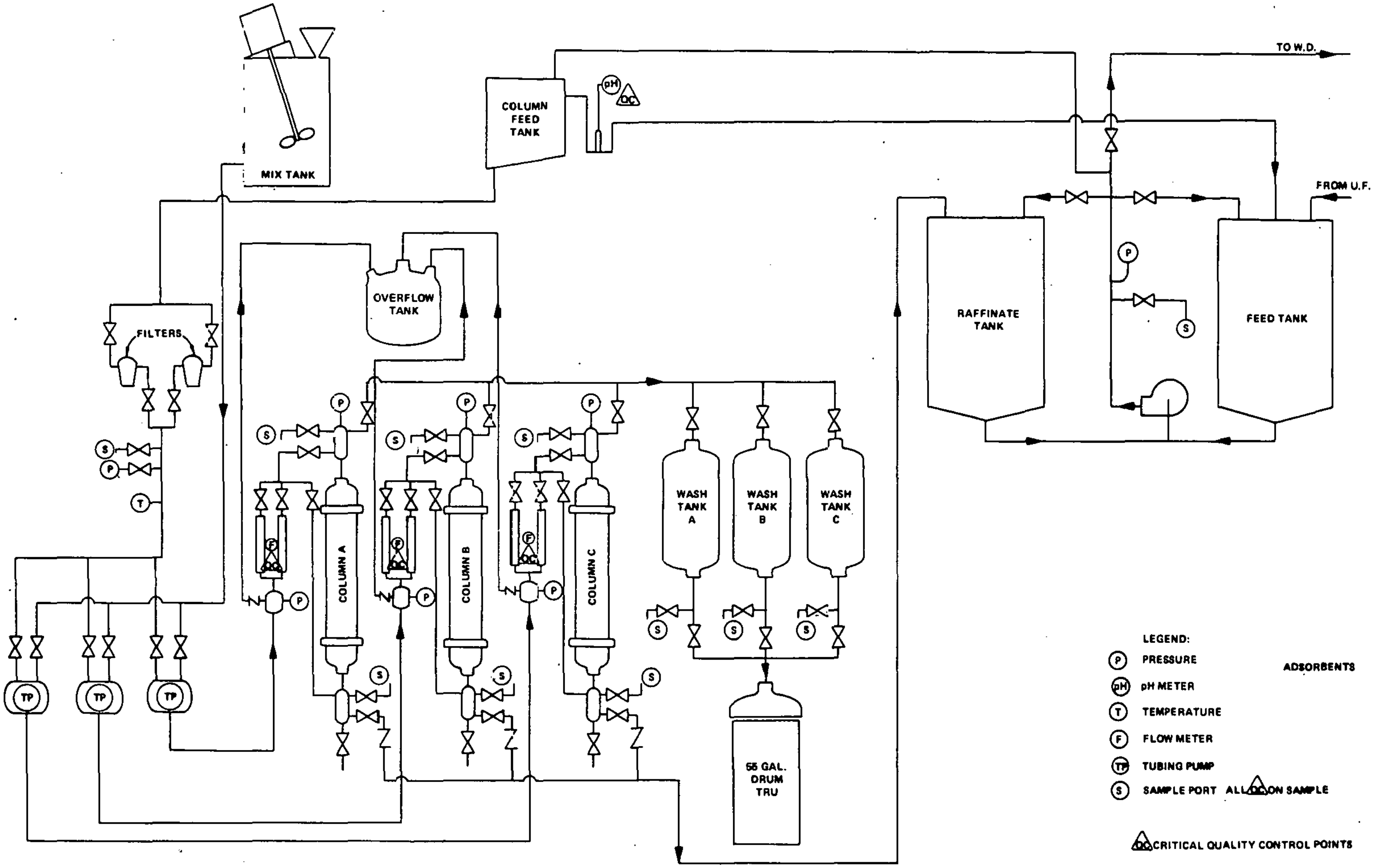


FIGURE 2 - Inorganic absorbents process flow diagram.

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