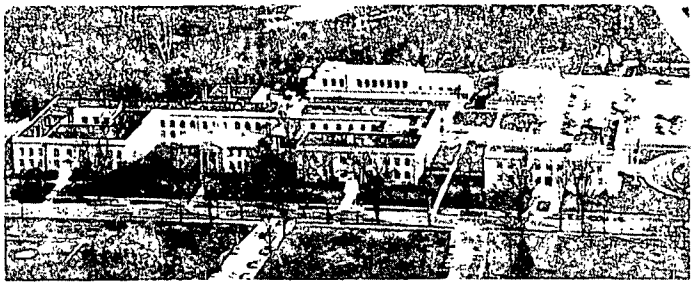

THE INSTITUTE OF PAPER CHEMISTRY, APPLETON, WISCONSIN

DEVELOPMENT OF A MANUFACTURING PROCEDURE FOR LOW-LITHIUM, LOW-URANIUM CONTENT FILTER PAPER

Project 3101

Report Three

A Status Report

to

DEPARTMENT OF THE AIR FORCE
1155th TECHNICAL OPERATIONS SQUADRON (HQ. COMD.)
McCLELLAN AFB, CALIFORNIA

January 12, 1973

THE INSTITUTE OF PAPER CHEMISTRY

Appleton, Wisconsin

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SUMMARY

Cotton linter pulp, Hercules PS-57, was leached with 2% solutions of nitric, hydrochloric, and hydrofluoric acids. All three acids appear to be equally effective in reaching a goal of < 0.3 ng. U/g. of pulp. Hydrofluoric acid was the most effective in removing lithium, but the average lithium content was 0.7 ng./g. of pulp, a larger residue by a factor of two than the goal sought.

A large batch of pulp (260 g.) in the form of a column was leached with hydrofluoric acid and washed with water. The bottom zone of the purified pulp contained 0.5 ng. Li/g. of pulp, the lowest level yet achieved for a purified pulp. The acid-free effluent from the column analyzed 0.013 ng. Li/ml., among the lowest in lithium of any process water or filtrate.

Data furnished for IPC-1478 filter paper, processed at the Central Laboratory, McClellan AFB, showed that hydrochloric acid at pH 3 followed by ammonium carbonate at pH 9 lower the contents of both uranium and lithium and that the presence of Kronisol did not interfere with the purification process. However, the purified paper retained amounts of both elements, especially lithium, in excess of the levels required.

INTRODUCTION

Based on the results obtained previously on Project 3101 (1, 2), efforts were directed toward (a) improvement of the quality of the water for processing the cellulose pulps, and (b) the comparison of nitric, hydrochloric, and hydrofluoric acids in the removal of uranium and lithium.

By leaching pulps with hydrofluoric acid it has been possible to lower the level of uranium to < 0.1 ng./g. of pulp. However, lithium is more persistent than uranium and the goal of < 0.4 ng. Li/g. of pulp has not been reached. The results reported herewith reinforce the results obtained previously for the removal of uranium and lithium (1, 2).

DISCUSSION

DEIONIZED WATER

The uranium contents and the 8/5 ratios for pulps purified with hydrofluoric acid or sodium fluoride (3101-011 to -015 and -018 to -023) (1, 2) suggested that the uranium originally present in the pulp was being removed and that the residue in the purified pulp may have been scavenged from the traces present in the wash water. Furthermore, the uranium and lithium contents of the IPC deionized water (3101-008) was practically the same as double-distilled water (3101-007, from a glass still) (1). Guided by these results and based on the assumption that lithium may be more tenaciously held by the cellulose than uranium, a back-up cartridge of a mixed-bed resin, in a stainless steel canister was placed in series with the deionized water supply. Effluent from the back-up cartridge was used in Samples 3101-027 to -058. The lithium and uranium data are summarized in Table I. A comparison of the dionized feed water (3101-026) with the effluent (3101-027) from the back-up cartridge, with respect to lithium, indicated that the mineral content of the feed water may have been inordinately high and suggested that a raw water break-through may have occurred in the IPC dionized water system. However, the uranium data suggested no such effect, but in order to guard against such accidental contamination and to lower the lithium level still further, two additional cartridges of deionizing resins have been connected in series.*

*Ion exchange resins: Research Cartridge No. 1506-30, and Puritan Cartridge No. 1506-40, Cole Parmer Instrument Co., Chicago, Illinois.

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TABLE I

LITHIUM CONTENT OF IPC SAMPLES
(3rd Shipment)[a]

IPC Sample No.		Description[b]		Lithium ng./ml.	Lithium ng./g.	Uranium 8/5	Uranium ng./g.	Uranium ng./ml.
3101-026		Deionized water from tap in Room 209	A (teflon beaker)	0.97[d]		129		0.00082
			B (Pt. dish)	1.06		135		0.00056
-027		Double-deionized water (effluent from a cartridge of mixed bed resin fed from deionized water tap in Rm. 209)	--[c]	0.021		126[d]		0.00069[d]
-028		2% nitric acid reagent		0.014		124[d]		0.0011[d]
-029		Filtrate (1 liter) from 2% nitric acid treatment of pulp (030-034)	A (teflon beaker)	0.14		115[d]		0.088[d]
			B (Pt. dish)	0.14		115[d]		0.069[d]
-035		Water washings (1 liter) from pulp after 2% nitric acid leaching		0.013				
-030	Circle 1 (top)	Stack of pulp circles			5.33			
	Circle 2	(73.7 g.) leached with			1.58			
-032	Circle 6	2% nitric acid; washed			0.78			
	Circle 7	with water; dried			1.21	138	0.113	
	Circle 8				1.15	130	0.209	
-034	Circle 11				0.90	135	0.269	
	Circle 12 (bottom)				1.62	125	0.123	
-035		2% hydrochloric acid reagent		0.017		134[d]		0.0011[d]
-037		Filtrate from 2% hydrochloric acid treatment of pulp		0.144				
-043		Water washings from pulp (038-042) after 2% hydrochloric acid leaching	A (teflon beaker)	0.015		127[d]	0.0018[d]	
			B (Pt. dish)	0.015		127[d]	0.0015[d]	
-038	Circle 1 (top)	Stack of pulp circles			2.67			
	Circle 2	(74.0 g.) leached with			1.00	127	0.157	
-040	Circle 6	2% hydrochloric acid;			1.19			
	Circle 7	washed with water;			1.17			
	Circle 8	dried			1.01			
-042	Circle 11				1.56			
	Circle 12				1.17	124	0.097	
	Circle 13 (bottom)				1.19			
-044		2% hydrofluoric acid reagent		0.018				
-045		Filtrate from 2% hydrofluoric acid treatment of pulp (046-050)		0.234		116[d]		0.140[d]

TABLE I (Continued)

LITHIUM CONTENT OF IPC SAMPLES
(3rd Shipment)[a]

IPC Sample No.		Description[b]		Lithium ng./ml.	Lithium ng./g.	Uranium 8/5	Uranium ng./g.	Uranium ng./ml.
-051		Water washings from pulp after 2% hydrofluoric acid leaching		0.018		123[d]		0.0085[d]
-046	Circle 1 (top)	Stack of pulp circles (111.1 g.) leached with 2% hydrofluoric acid; washed with water; dried			2.56			
					0.89			
-048	Circle 9				0.69			
	Circle 10				0.71			
	Circle 11				0.79			
-050	Circle 18				0.59			
	Circle 19				0.66			
	Circle 20 (bottom)				0.79			
-052		Circles of pulp leached with 2% hydrofluoric acid followed by 0.05% hydrofluoric acid; not dried before shipment; dried at MCL	A		0.90			
			B		1.01			
			C		1.12			
-053		Water filtrate (2 l.) from the dispersion of 260 g. of pulp in 4 l. of water		0.20				
-054		Filtrate (2 l.) from 2% hydrofluoric acid leaching of 260 g. pulp (056-058)		0.117				
-055		Water effluent from purified pulp (056-058)		0.013				
-056	Top zone	Hercules P5-57 pulp, 260 g., leached with 2% hydrofluoric acid; washed with water; dried	A		1.23			
			B		1.19			
-057	Middle zone		A		1.04			
			B		0.79			
-058	Bottom zone		A		0.56			
			B		0.48			

[a] All analytical data were obtained at the McClellan AFB, MCL-C, and were transmitted in a letter dated December 21, 1972, from Captain James R. Wright to E. E. Dickey. Results for uranium are incomplete and will be reported in future reports.

[b] In this report "pulp" refers to Hercules P5-57 cotton linters.

[c] All unspecified analyses were ashed in platinum dishes.

[d] Hand-calculated values, awaiting computer calculations and printouts.

These resins are designed to yield water of extraordinary purity when used with a feed water of ordinary deionized or distilled water. Analytical data should be available early in 1973 on water thus purified.

PURIFICATION OF PULP WITH STRONG ACIDS

Because 2% hydrofluoric acid was successful in reaching the goal for the uranium content of cotton linter pulps, the process was repeated with 2% hydrochloric and nitric acids. A comparison of the analytical results, Table I, Samples 3101-030 to -034, -038 to -042, and -046 to -050 shows that these acids may be equally effective in removing uranium. Somewhat in contrast, the data for lithium suggest that hydrofluoric acid was considerably more effective than either nitric or hydrochloric acids. Even so, the average lithium content in pulps leached with hydrofluoric acid, uncorrected for a blank, was 0.7 ng. Li/g. of pulp, an amount nearly twice the goal sought. Because the wash water exposed the pulp to 0.2-0.3 ng. of Li/g. of pulp, the lowering of the lithium content in future work may aid our progress toward the goal required (< 0.4 ng. Li/g.).

One sample (3101-052) of pulp leached with hydrofluoric acid was not dried in the usual way but was wrapped in polyethylene, and submitted for analysis. The lithium content, 1.0 ng. Li/g., was surprisingly high, but the reason for the unexpected amount of lithium is unknown.

The experiment may be repeated with added precautions to diminish the possibility of accidental contamination.

PURIFICATION OF PULP WITH HYDROFLUORIC ACID. LARGE BATCH

Based on the effectiveness of the percolation technique experienced with circles of dry-lapped pulp, an experiment was performed with 260 g. of pulp which had been dispersed in water and collected as a thick mat or column (14.5 cm. in diameter x 13 cm. in height). The column of pulp was leached with 2% hydrofluoric acid followed by water until the washings were no longer acidic (Congo Red paper). Representative samples of the purified pulp (3101-056 to -058) and the aqueous filtrates (3101-053 to -055) were collected for analysis. As shown in Table I, the water washings from the purified pulp was the lowest in lithium of all aqueous samples in this series. This would be expected because the pulp, purified by acid, was capable of sequestering traces of cations from the process water. Furthermore, the lowest lithium values obtained thus far for pulp samples were recorded for the bottom zone (3101-058) of the purified column. This is consistent with the ion-exchange behavior of cellulose.

IPC-1478 FILTER PAPER PROCESSED BY McCLELLAN AFB, MCL-C

Two experiments with IPC-1478 filter paper, untreated with Kronisol, involved washing with hydrochloric acid at pH 3 followed by ammonium carbonate at pH 9 with water-washing after each step. The results for lithium are summarized in Table II. A comparison of the washed paper with control samples indicated that approximately half the lithium initially present had been removed. This result is in general agreement with the results for similarly processed IPC-1478 paper containing Kronisol (2), and suggests that the Kronisol may not hinder the removal of lithium by such washing processes.

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TABLE II

LITHIUM CONTENT OF IPC-1478

Filter Paper (Untreated with Kronisol)
After Chemical Purification

Experiments and analyses performed
by the McClellan AFB, MCL-C

MCL-C No.	Description		Lithium, ng./g.	Uranium[a] 8/5	Uranium[a] ng./g.
Control	June, 1970		7.53		
012-5538 control	November, 1972	A	8.62		
		B	8.95		
012-5539	Scrim removed; stack of ten circles leached with hydrochloric acid at pH 3, water-washed, leached with ammonium carbonate at pH 9, water-washed, dried.	A	4.71	125	0.363
		B	(7.96)	(99)	(0.612)
		C	4.32	108	0.332
		D	5.00		
		E	4.32		
		F	5.36		
		G	4.93		
		H	5.44		
		I	4.82		
		J	4.74		
012-5540	Same experimental conditions as in 012-5539 above except that the scrim was removed after processing the circles.	A	4.93		
		B	4.80		
		C	4.60		
		D	4.87		
		E	5.87		
		F	5.12		
		G	5.10		
		H	5.50		
		I	4.02		
		J	4.18		
	Process water, double-distilled.		0.015 ng./ml.		

[a] Hand-calculated values, awaiting computer calculations and printouts.

FUTURE WORK

1. Attempt to produce process water for Project 3101 which contains < 0.01 ng. Li/ml. Then, pulps processed at 5% consistency (5 g. pulp/100 ml. of process water) would be exposed to lithium at < 0.2 ng./g. of pulp. If an acid treatment can remove enough of the lithium originally present, the goal of < 0.4 ng. Li/g. in the final IPC-1478 filter paper may be achieved.

2. Process Hercules PS-57 pulp and IPC-1478 filter paper (untreated with Kronisol) with the improved process water.

3. Attempt to exchange sodium for lithium and then remove the metal with hydrofluoric acid. This experiment may reveal whether or not lithium and sodium are exchangeable in the purified pulp.

EXPERIMENTAL

DEIONIZED WATER

Appleton city water is fed into a mixed bed resin deionizer and the processed water is distributed through polyethylene tubing with stainless steel fittings to a number of the laboratories in one section of the Institute. Sample 3101-026 was bottled at the tap in Room 209, the laboratory in which most of the work on Project 3101 is performed.

DOUBLE-DEIONIZED WATER

Deionized water from the tap in Room 209 was fed into a cartridge (stainless steel) of Amberlite mixed bed resin to assure that the mineral content of the water would be as low as possible. Sample 3101-027 was bottled from the effluent of the back-up cartridge.

PURIFICATION OF PULP WITH NITRIC ACID

A stack of 12 circles (73.7 g.) of Hercules PS-57 pulp was packed on a polyethylene Buchner funnel and 1.0 liter of 2% nitric acid (20.0 ml. of concentrated nitric acid diluted to 1.0 liter) was percolated through the stack under gravity. The acid was added in several portions over a period of 60-90 minutes. The stack was washed with 1.0 liter of water, pressed by a rubber dam under a partial vacuum (water aspirator), the circles were separated, numbered, and air-dried at room temperature under a current of filtered air. The reagent and filtrates were sampled, and the circles of pulp were grouped and numbered for analysis.

Sample No.	Description
3101-028	2% Nitric acid reagent
-029	2% Nitric acid filtrate from the pulp (030, etc.)
-035	Water washings after the nitric acid treatment
-030	Circles 1 (top), 2
-031[a]	Circles 3, 4, 5
-032	Circles 6, 7, 8
-033[a]	Circles 9, 10
-034	Circles 11, 12 (bottom)

[a]Not analyzed; retained by IPC.

PURIFICATION OF PULP WITH HYDROCHLORIC ACID

A stack of 13 circles (74.0 g.) of Hercules PS-57 pulp was leached by percolation with 1 liter of 2% hydrochloric acid followed by 1 liter of water according to the general procedure described for the nitric acid purification (see above). The following samples were collected.

Sample No.	Description
3101-036	2% Hydrochloric acid reagent
-037	2% Hydrochloric acid filtrate from the pulp (-038, etc.)
-043	Water washings after the hydrochloric acid treatment
-038	Circles 1 (top), 2
-039[a]	Circles 3, 4, 5
-040	Circles 6, 7, 8
-041[a]	Circles 9, 10
-042	Circles 11, 12, 13 (bottom)

[a]Not submitted for analysis; retained by IPC.

PURIFICATION OF PULP WITH HYDROFLUORIC ACID

A stack of 20 circles (111.1 g.) of Hercules PS-57 pulp was leached by percolation with 1 liter of 2% hydrofluoric acid followed by 1.5 l. of water according to the general procedure described for the nitric acid purification (see above). The following samples were collected.

Sample No.	Description
3101-044	2% Hydrofluoric acid reagent
-045	2% Hydrofluoric acid filtrate from the pulp (-046, etc.)
-051	Water washings from the hydrofluoric acid treatment
-046	Circles 1 (top), 2
-047[a]	Circles 3, 4, 5, 6, 7, 8
-048	Circles 9, 10, 11
-049[a]	Circles 12, 13, 14, 15, 16, 17
-050	Circles 18, 19, 20 (bottom)

[a]Not submitted for analysis; retained by IPC.

PURIFICATION OF PULP WITH HYDROFLUORIC ACID, WITHOUT WASHING OR DRYING THE PULP

A stack of 6 circles of Hercules PS-57 pulp was leached with 500 ml. of 2% hydrofluoric acid followed by 500 ml. of 0.05% hydrofluoric acid (strongly acid to Congo Red). The pad was then pressed under a rubber dam in the usual way. Without drying, the third, fourth, and fifth circles were packaged as a single sample in polyethylene and were submitted for analysis, numbered 3101-052.

PURIFICATION OF PULP WITH HYDROFLUORIC ACID. LARGE BATCH

A large polyethylene bottle was fashioned into a percolation tube, 14.5 cm. in diameter and 20 cm. in height. The bottom was trimmed, perforated with 1/16 inch holes, and placed in the inverted bottle as a septum. Hercules pulp, PS-57, was dispersed in water and poured into the tube in two 80 gram-lots and two 50

gram-lots for a total of 260 g. of airdry pulp. A total of 4 l. of water was used for the dispersion of the pulp. This involved the reuse of the filtrate as each lot was dispersed and added to the column. The charge of pulp formed a loosely compacted column 13 cm. in depth. After the final addition of pulp, 2 l. of filtrate was collected and numbered 3101-053. Two liters of 2% hydrofluoric acid was then percolated through pulp and 2 l. of acid filtrate was collected and numbered 3101-054. The pulp bed was then washed with water until free of acid (Congo Red paper), after which a sample was collected for analysis, 3101-055. A total of 4.5 l. of water was required following the acid in order to collect 1 liter of acid-free effluent. Pulp was removed from the top, middle, and bottom zones of the column of pulp, pressed under a rubber dam, and dried in an oven at 50° under gravity circulation of air.

Sample No.	Description
3101-053	Water filtrate (2 l.) from the dispersion of 260 g. of pulp
-054	2% Hydrofluoric acid filtrate (2 l.) from 260 g. pulp
-055	Acid-free water effluent from the purified pulp
-056	Top zone
-057	Middle zone
-058	Bottom zone

LITERATURE CITED

1. Project 3101, Report One, September 29, 1972.

2. Project 3101, Report Two, November 10, 1972.

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