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SEPARATION OF PHOSPHORUS^{32} FROM SULFUR^{32}

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ABSTRACT

Carrier-free radioactive phosphorus can be prepared in the pile by (n,p) process on sulfur^{32}.

$$_{16}S^{32}(n,p)_{15}P^{32} \qquad {}_{15}P^{32} \xrightarrow[14.3d]{1.7\ Mev} {}_{16}S^{32}\ (stable)$$

There are no by-products in this material except those formed from nuclear reactions of the chemical contaminants.

$$_{16}S^{32}\ (n,d)\ {}_{14}Si^{31} \xrightarrow[170m]{1.8\ Mev} {}_{15}P^{31}$$

About 2 kg of specially purified sulfur is irradiated in a large aluminum can in the pile for a period of at least six weeks. The contents of the can are melted out, and the active phosphorus is extracted with weak nitric acid under pressure at a temperature greater than 120°C employing mechanical agitation. The waste molten sulfur and the active phosphorus extract are separated, and the latter is processed in order to remove chemical contaminants. Thus carrier-free active phosphorus produced in the Clinton pile is chemically separated from sulfur in multi-millicurie quantities.

CONCLUSIONS

Yield

Little may be said about the extraction yield of P^{32} because of the inconsistency of analytical results of P^{32} contained in the starting sulfur. In like manner, analyses of the extracted sulfur for P^{32} are very poor. Therefore, the only notable analysis regarding extraction yield is that of the P^{32} extract of which an average of 85.4 per cent is recovered by volume as shown in Table 1. Figure 1 indicates that at least 1500 mc P^{32} are available from 2000 g of 75 per cent saturated material. These data are based on material of 75 per cent saturation, which represents the optimum irradiation period of six weeks and decay period of three days for safe handling.

Adequate data on purification yield are not available at this time since few runs have been made in the Cell 5 glass equipment. Furthermore, modifications to the purification process are yet in progress Relatively low yields, based on the amount of P^{32} in the extract, in the order of 40 per cent have been obtained. However, with recent improvements, it is anticipated that yields in the order of 80 per cent will be reached.

Contaminants

The chief contaminants contained in the extract are the main constituents of stainless steel, namely, iron, chromium, and nickel. Corrosion of the stainless steel extraction equipment occurs from sulfuric acid which is formed by the action of nitric acid on sulfur.

Shown on Figs. 2, 3, and 4 are the relationships of corrosion product pickup to acid concentration. Specifications of allowable corrosion products were not given at the start of the project, although it was known that iron would not be critical since this material was used for carrying P^{32} in the purification procedure. Nickel was fairly easily removed from the extract, but chromium, most of which was absorbed by the Nalcite resin, held up large quantities of activity.

From the curves shown in Figs. 1, 2, 3, and 4, it may be concluded that 0.2M nitric acid is the optimum concentration for the greatest removal of P^{32} from sulfur with a minimum of corrosion products in the extract. It may be noted that by increasing the acid concentration from 0.2 to 0.3M, the increase in P^{32} extracted is only 15 per cent, whereas, the corresponding increase in corrosion products is 70 per cent, 175 per cent, and 75 per cent respectively for iron, chromium, and nickel. But by lowering the acid concentration to 0.1M, the small decrease in corrosion products does not offset the very large drop in the amount of P^{32} extracted.

Aluminim was usually found in the extract but was easily removed in the resin column by absorption.

Small amounts of silica were noted after the final evaporation of the product solution. A fine sintered glass filter disc was employed for removing this precipitate.

Specification of the final product solution is given below:

Total solids	10 mg/ml
Nonvolatile matter	5 mg/ml
Chlorine	5 mg/ml
P^{32} concentration	0.5 mc/ml
Carrier	25μg of P as (H_3PO_4) /mc P^{32}
pH	7 to 9 (must show no precipitate)

Adequate Process

The process as described in this report is considered to be adequate with regard to design, operation, and safety for the production of P^{32} from S^{32}. The yields obtained on the purification of the extract are inefficient, but recent work with lanthanum as the carrier in place of iron assures greatly improved yields.

DISCUSSION

History

In 1944, the initial work on the extraction of P^{32} from S^{32} was started by the Biology Department of Clinton Laboratories. A process was developed whereby P^{32} was atmospherically extracted with fuming nitric acid from a 1 lb sample of S^{32} irradiated in the Clinton pile. From the data obtained, 500 mc of P^{32} were reported to be available from 2 kg of sulfur.

In 1945, the Chemistry Division proceeded to develop a pressure extraction process in an attempt to improve the extraction efficiency and reduce the hazards associated with the atmospheric process. Experimental work continued until the summer of 1946 at which time the responsibility of the work was assumed by the Technical Division Operations Area.

The equipment which was installed in Cell 3 of Building 205 consisted of an extractor constructed of Hastelloy with auxiliary pressure vessels for melting out 2 kg of sulfur and transferring it to the pressure extractor. The liquid-liquid extraction was carried out under pressure with weak nitric acid and mechanical agitation. The sulfur was allowed to solidify and the extract decanted. Although accurate operating conditions were not determined during the few months of operation, considerable data were obtained from which a new plant was designed and later set up in Cell 5 of Building 205.

Due to equipment failure, and purification difficulties as the result of excessive amounts of corrosion products formed, experimental runs in Cell 3 were discontinued later in 1946. Plans for installing newly designed equipment in Cell 5 were speeded up.

Meanwhile, atmospheric extraction of P^{32} was carried out with fuming nitric acid in glass equipment in Building 706-D. This process was inefficient and extremely hazardous but served as the only source of carrier-free P^{32} until April of 1947 when the first active extraction was made in Cell 5.

Chemical Process and Chemistry

Carrier-free P^{32} is extracted from the sulfur with 0.2M molar nitric acid at a temperature between 120°C and 140°C and a pressure between 20 psi and 40 psi. The 2 kg of sulfur are melted out of the aluminum can into the transfer vessel, over a period of 2 hr. One liter of 0.2M nitric acid is added to the cold extractor and raised to the temperature and pressure ranges stated above by applying 65 psi steam to the jacket of the extractor. The molten sulfur is added to the nitric acid by equalizing pressures in the extractor and transfer vessel. The two phases are mechanically agitated for one and one-half minute and allowed to settle for 20 min. The P^{32} and some S^{32} are oxidized to $PO_4^=$ and $SO_4^=$ during this time.

The sulfur phase is removed from the extractor followed by the acid phase which is collected in a separate receiver. The extracted sulfur is drawn off into a closed container and discarded. The acid phase is filtered through a coarse crud filter to a transfer vessel from which the solution is dropped to a Stang reactor in the glassware hood.

The Group III and Group IV cations, should the latter be present in the extract, are removed by a hot sodium hydroxide precipitation while the product remains in the filtrate. The product solution is then acidified with hydrochloric acid, and Fe^{+++} as $FeCl_3$ added to carry the product as FeP^*O_4 precipitated by ammonium hydroxide.

The product precipitate is dissolved in hydrochloric acid, adjusted to 0.1M, and passed through the Naclite resin column, which absorbs the Fe^{+++} and Al^{+++}. The product solution is evaporated to dryness to remove chlorides, and the product taken up with an amount of water such that the P^{32} concentration is not below 1 mc/ml. The solution is adjusted to a pH of 7.2 to 8.0 with sodium hydroxide and filtered through a fine glass disc to remove any silica or foreign matter that might be present.

Should noncarrier-free P^{32} be desired, 0.025 mg of P^{31}/mc is added to the solution prior to evaporation.

Of great importance is the new purification process developed by the Chemistry Division and used by the Operating Department for the last few runs. The process, which employs lanthanum instead of iron as the carrier, appears to be highly satisfactory. The chemical flow diagram as shown below employing lanthanum represents essentially the same process as that for iron.

Design of Equipment

The design of the P^{32} extraction equipment in Cell 5 was based primarily on the experimental data obtained in the operation of the equipment in Cell 3. Arrangement of the equipment is essentially the same with the added feature of separating the sulfur in a molten state from the acid phase. The equipment is designed to handle three cans of sulfur per extraction although only one can at a time has been processed to date.

The main vessels are constructed of 25-12 SCb with 18-8 SCb jackets and process piping. All of the vessels are designed for 60 psi working pressure except the sulfur melter, which operates under atmospheric pressure. All vessels, process piping, and process valves are either steam or electrically heated in order that the temperature at any point in the process may be kept above 120°C, the approximate melting point of sulfur. The sulfur melter and the extract and sulfur receiver drain valves are electrically heated and controlled by variacs. The control of the sulfur melting is fully automatic while the latter are manually controlled. All remaining vessels are jacketed around the sides and on the bottoms, while the process lines and valves are steam traced with copper tubing. Sixty-five psi steam is maintained on the above equipment and lines by a steam regulating valve which eliminates manual control of individual steam valves.

The proper functioning of the electrode assembly located in the draw-off line from the extractor is of prime importance in regard to recovery of the P^{32} extract. The chief problem of insulating two platinum wires which extend into the 3/8 in. IPS line, from the pipe and body of the assembly, and withstanding an internal pressure of 60 psi without leaking, was accomplished by using Teflon. External pressure is applied to the Teflon packing rings by a gland nut.

The safety features of the extraction equipment consist of a remotely located air jet for venting the equipment containing contaminated air. The equipment in itself provides sufficient shielding against radiation.

With the exception of placing the sulfur can in the melter and removing same, all transfers of active materials are carried out by remote control with adequate shielding. The entire glassware operations are carried out behind 1/2 in. Lucite shielding.

Incorporated in the design are catch pans and "hot" drain lines for waste disposal and decontamination purposes.

Construction

Project C-191-M, Separation of P^{32} from S^{32}, was requested August 27, 1946, and approved by USED August 29, 1946, prior to completion of the final drawings. Cell 5 was stripped of all equipment, and cleaned, and a new concrete floor was poured with several new waste lines to the center floor drain.

Fabrication of equipment was started as drawings were completed but progress was rather slow. In early December, installation of the equipment was started and completed about February 1, 1947. This delay was primarily due to the fact that another project in the cell was given higher priority on construction, and that shipment of the Lightnin' Mixer agitator was delayed.

The hood for the glass purification equipment was installed in June, and, after several changes and modifications due to the unsettled state of the purification process, the glassware was installed in early July.

Operations

Due to the urgent need of retiring the hazardous fuming nitric acid atmospheric process, the problem of determining the maximum period of agitation for a fixed settling time to give an extract recovery of 80 per cent or better seemed foremost. Several runs with inactive sulfur and weak nitric acid were made for this determination, and analyses of the extracts indicated that the total mixing and settling time probably would have to be reduced to prevent excessive corrosion. (See Table 1, Runs 6 to 11).

Several more runs with inactive sulfur and weak nitric acid were made at the reduced settling period of 20 min, and a maximum mixing time was determined to give an extract recovery of 80 per cent or better. Corrosion products were reduced substantially. (See Table 1, Runs 13 to 18).

With the mixing time and settling time fixed, the third important variable, the nitric acid concentration, was studied by using about 10 per cent active sulfur with inactive sulfur in the next series of runs. Due to a complete lack of data on the irradiation time of the active sulfur used, the results were of little value until April 17, when the first full can of active sulfur on which complete irradiation data were known was processed.

Since that time, the strength of acid used for extraction was the only operating variable in the process. (See Table 2). Because the temperature of the extractor could not be accurately controlled during the mixing and settling periods, the temperature in all runs was considered to be constant, although the range was 120 to 140°C.

Operation of the glass equipment is satisfactory in every respect. Periodic replacement of sintered glass filters is necessary due to their plugging by precipitates.

Results

The results of 35 active extractions at constant mixing and settling times are shown in Table 2. The nitric acid concentration was varied from 0.05M to 0.6M in an effort to show the maximum quantity of P^{32} available from 2 kg of sulfur. It is felt that insufficient data were obtained in the higher acid concentration range, and for this reason, the curves plotted in this range are shown by dotted lines on Figs. 1, 2, 3, and 4. Further investigation at higher acid concentrations was desirable, but was deemed impracticable in view of the ever increasing demand for meeting shipping requirements and the low purification yields when excessive corrosion products were present.

Correlation of results is good considering the possible errors in the calculated per cent saturation as a result of varying pile flux. There is also the probability that that portion of the acid phase in immediate contact with the molten sulfur layer during the settling period is more highly concentrated in P^{32}. This is based on the assumption that extraction at the interface takes place during the settling period. If this is true, the 15 per cent by volume of extract lost on the separation would be lower than the per cent activity lost. This reasoning indicates that the activity curve shown on Fig. 1 might be low.

The scattering of corrosion data is due partially to inefficient cleaning of the equipment prior to runs, and to variations in the extraction temperatures, although the latter effect could not be correlated.

The time cycle for a complete run is shown as follows (see the flow diagrams):

1. Melt sulfur from can in P_1 and collect in P_2 ---------- 2 hr
2. With acid up to temperature and pressure in P_3, equalize P_2 and P_3 ---------- 5 min
3. Agitate and settle contents of P_3 ---------- 25 min
4. Separate sulfur and extract by collecting in P_4 and P_5, and draining to disposal can and P_6, respectively ---------- 30 min

   Total for extraction ---------- 3 hr
5. Filter extract to TV-1 and precipitate corrosion products with NaOH in SR-1. Filter to TV-2 ---------- 1 hr
6. Transfer solution to SR-2, add carrier, and precipitate with NH_4OH. Filter waste to W-1, take up precipitate with HCl, and transfer to TV-3 ---------- 1 hr
7. Adjust molarity and transfer to TV-4. Run solution through resin column and evaporate to dryness ---------- 18 hr
8. Heat product at dryness for 30 min, take up with H_2O, and adjust pH ---------- 45 min
9. Filter solution to TV-5 and drop to burette ---------- 15 min

   Total for purification ---------- 21 hr

   Total time for complete run ---------- 24 hr

Table 1

Run No.	Mixing time, min	Settling time, min	Volume acid recovery, %	Corrosion products Fe, mg	Cr, mg	Ni, mg
6	4	60	50	41	40	8
7	4	60	70	*	*	*
8	3	60	57	*	*	*
9	2	60	75	255	8	3
10	2	60	77	154	12	34
11	1	60	80	70	7	6
13	1	20	80	45	5	0
14	2	20	71	11	6	3
15	1.5	20	88	5	1	1
16	1.5	20	85	21	1	3
17	1.5	20	87	26	1	3
18	1.5	20	87	44	3	1

*1.0M HNO_3 used; 0.1M HNO_3 used in other runs.

Table 2*

Run No.	Active sulfur,	Irradiation, T/T 1/2	Decay, T/T 1/2	Calculated saturation at extraction time, %	Nitric acid molarity	Extract recovered, vol. %	Total P^{32} in extract, mc	Total P^{32} Corrected to 75 % saturation and 100 % recovery extract	Total Fe in extraction corrected to 100 % recovery, mg	Total Cr in extract, mg	Total Ni in extract, mg
44	2000	1.47	0.28	53	0.05	89	127	202	61	1	20
52	2000	2.94	0.42	65	0.075	80	402	580	379†	19†	145†
35	1950	0.70	0.35	30	0.10	88	240	680	88	3	15
46	1990	2.94	0.21	75	0.10	75	664	880	108	24	8
53	2035	2.45	0.21	71	0.125	80	478	630	357†	56†	105†
54	2105	2.45	0.28	68	0.15	70	549	860	557†	34†	110†
28	2000	3.15	0.42	66	0.20	100	699	795	55	5	5
32	2145	0.49	0.42	22	0.20	92	333	1235	-	-	-
34	1950	0.70	0.35	30	0.20	93	309	832	156	13	21
38	1960	1.19	0.78	33	0.20	102	363	805	121	5	43
45	1991	4.61	0.35	75	0.20	77	845	1095	390	21	91
47	2000	4.40	0.49	68	0.20	98	739	830	199	86	49
60	2012	2.66	0.35	66	0.20	87	632	823	150	11	29
61	2000	1.96	0.42	55	0.20	91	735	1100	178	3	44
62	1995	2.45	0.28	68	0.20	100	1250	1380	219	2	55
29	2000	3.71	0.35	72	0.25	95	1428	1560	104	14	19
36	2000	3.71	0.84	51	0.25	84	884	1480	158	18	36
59	2040	2.66	0.28	69	0.25	57	649	1230	370	9	96
31	1993	0.49	0.42	22	0.30	94	375	1355	-	-	-
33	1955	0.70	0.28	31	0.30	99	395	965	200	25	30
40	1994	1.05	0.84	29	0.30	86	315	943	265	21	50
42	1950	4.61	0.21	83	0.30	84	1203	1295	300	24	52
49	1993	1.75	0.91	38	0.30	75	393	1040	433	28	183
57	2080	2.45	0.35	64	0.30	89	766	1010	550	38	60
58	2000	2.45	0.42	61	0.30	88	999	1390	294	20	85
63	2036	2.94	0.28	72	0.30	79	653	865	380	0	150
55	2147	2.45	0.35	64	0.35	84	800	1120	440	5	71
65	2000	2.45	0.42	61	0.35	82	680	1020	307	0	156
30	1992	1.47	0.21	55	0.40	91	810	1230	133	15	0
41	2000	4.90	0.21	83	0.40	88	1183	1215	381	40	70
48	2000	2.94	0.42	65	0.40	87	1179	1560	532	56	192
64	2000	2.45	0.35	64	0.40	77	935	1420	576	93	130
50	1995	1.75	0.98	34	0.50	73	443	1340	636	30	150
51	1920	2.94	0.35	68	0.50	79	948	1325	1445	110	385
56	2095	2.94	0.42	65	0.60	72	864	1515	1585	97	390

*1000 ml nitric acid and 100 ml water used for extraction and rinse in all runs. Mixing and settling times for all runs were 1 1/2 min and 20 min, respectively.
†Data not plotted because equipment was not properly cleaned prior to runs.

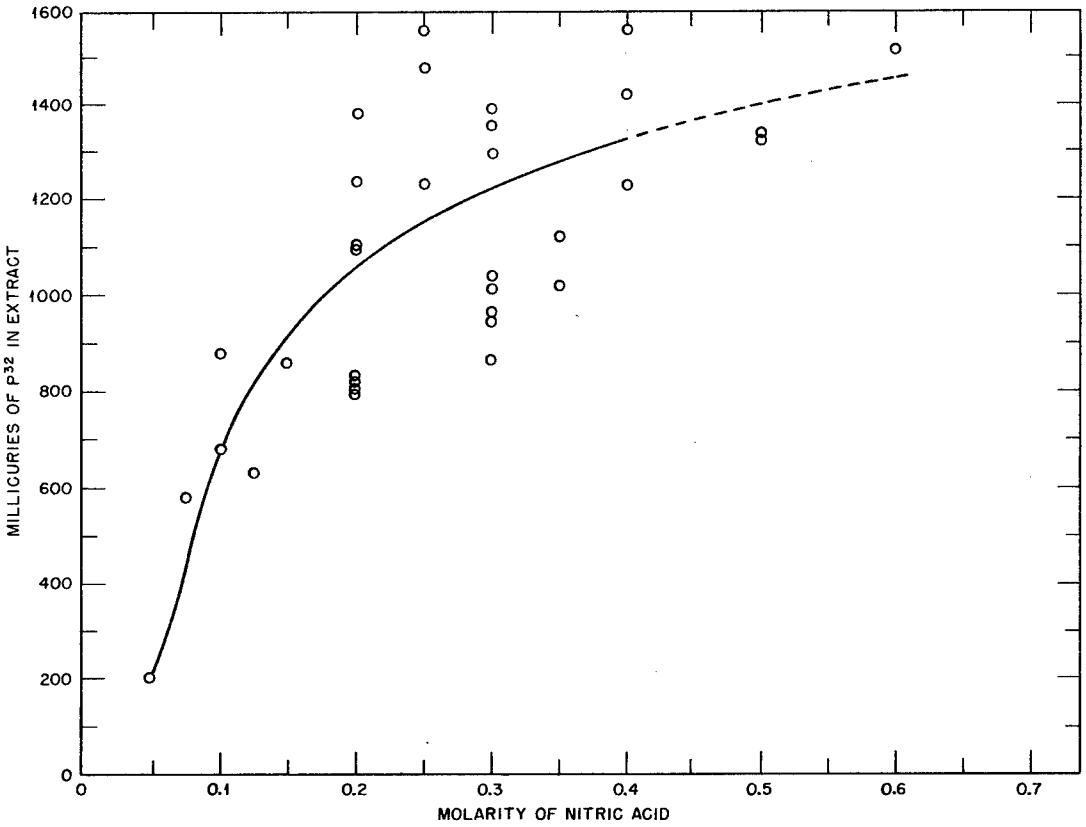

Fig. 1 — P^{32} extracted versus acid concentration. Values corrected to 75 per cent saturation and 100 per cent recovery of extract by volume.

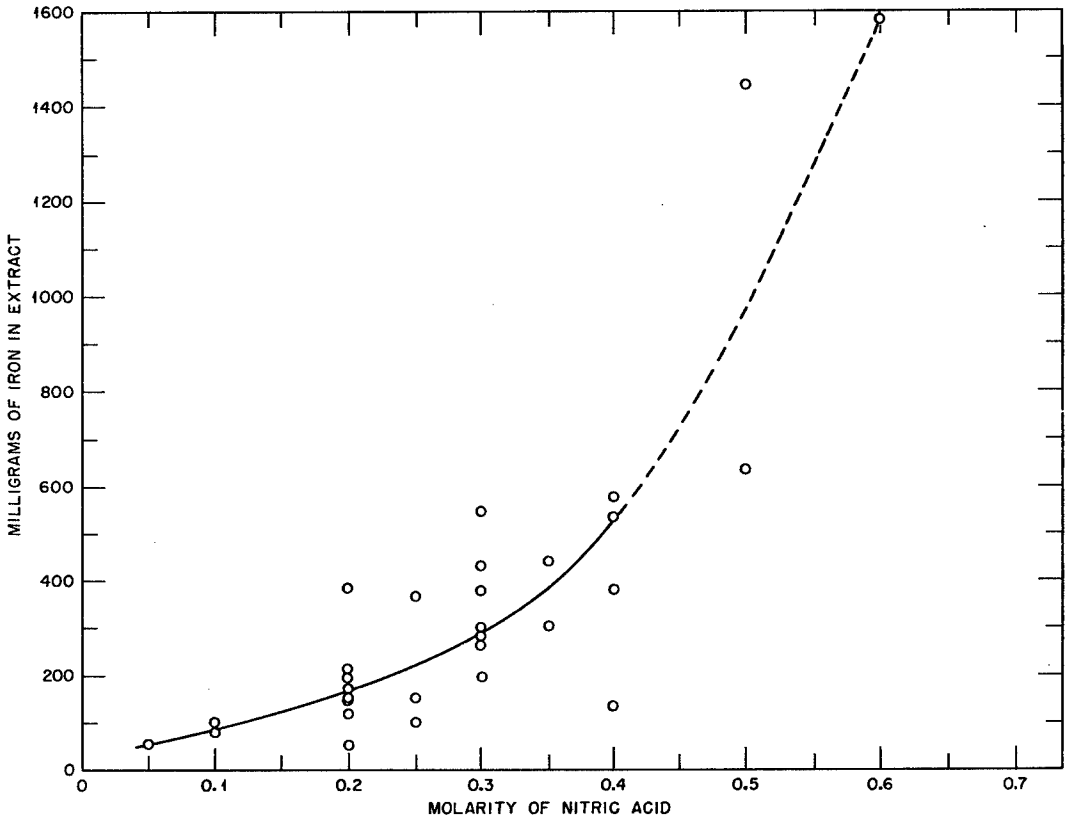

Fig. 2 — Corrosion product pickup versus acid concentration. Values corrected to 100 per cent recovery of extract by volume.

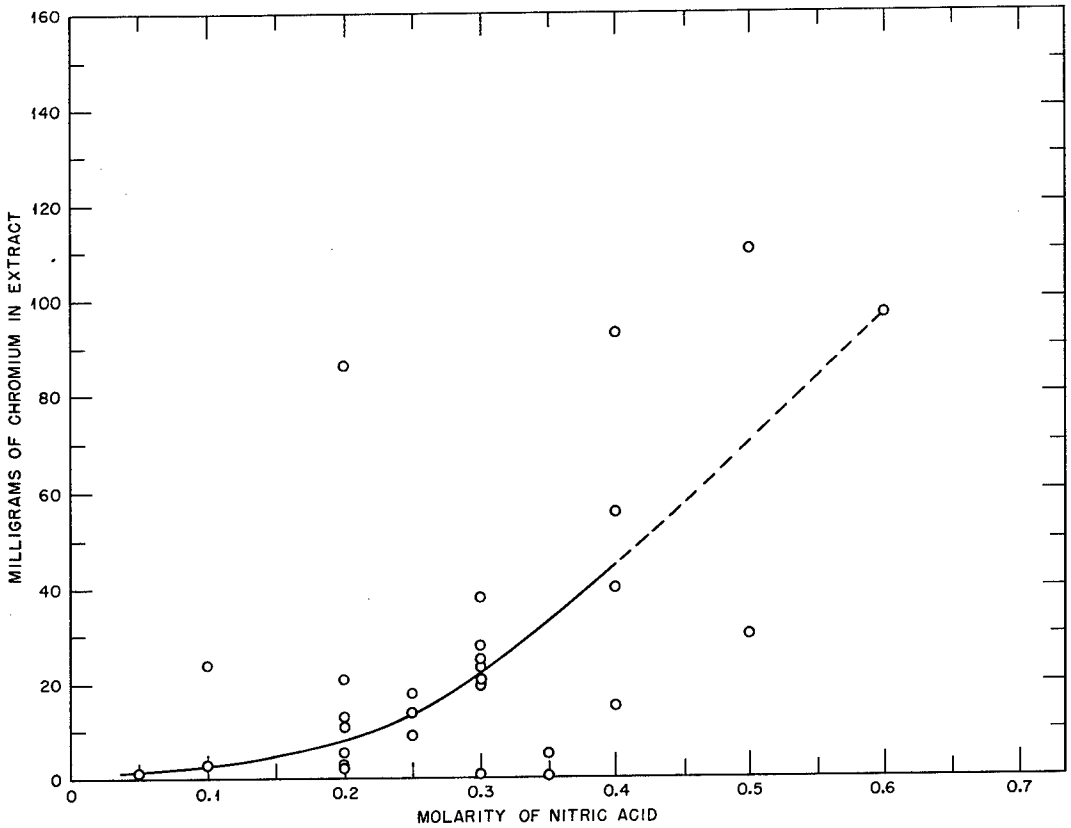

Fig. 3—Corrosion product pickup versus acid concentration. Values corrected to 100 per cent recovery of extract by volume.

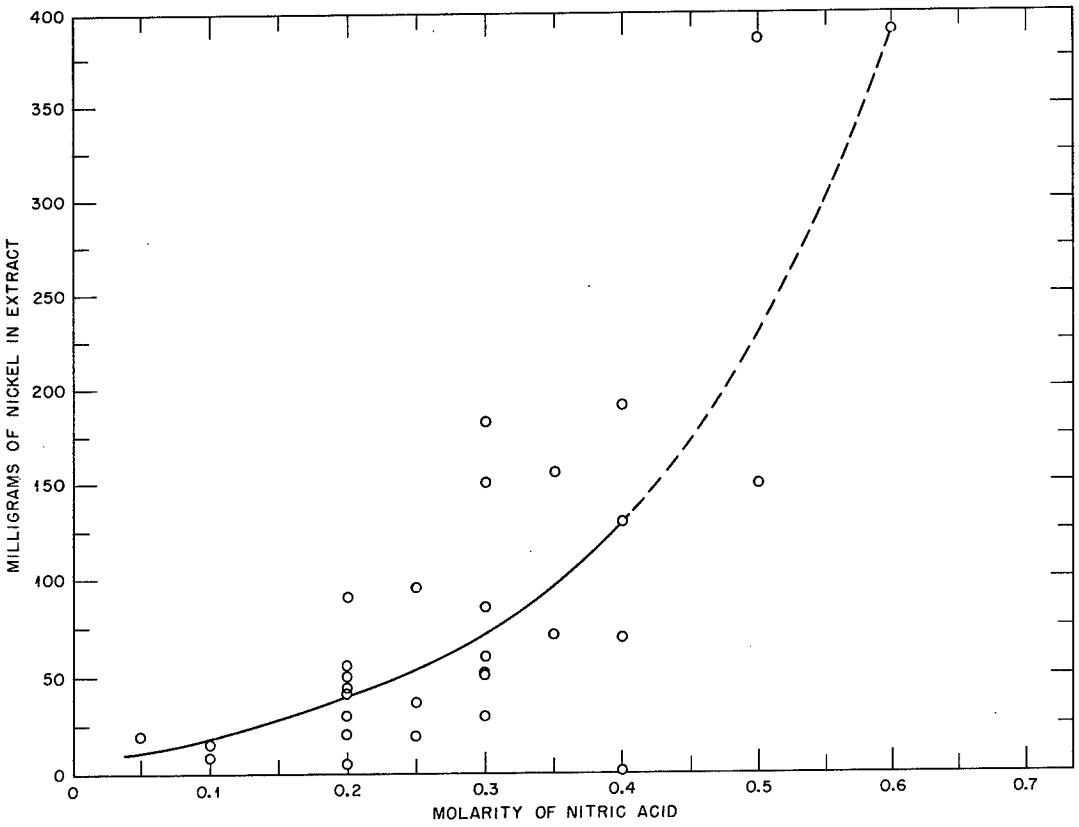

Fig. 4—Corrosion product pickup versus acid concentration. Values corrected to 100 per cent recovery of extract by volume.

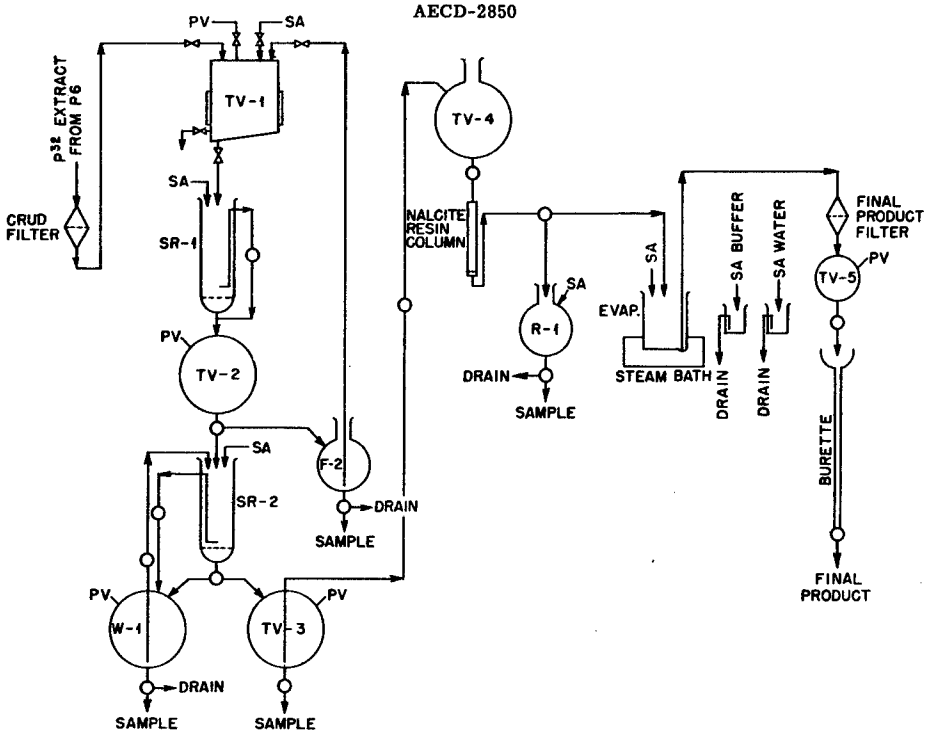

Fig. 5—Flow diagram of P^{32} purification equipment (Cell 5).

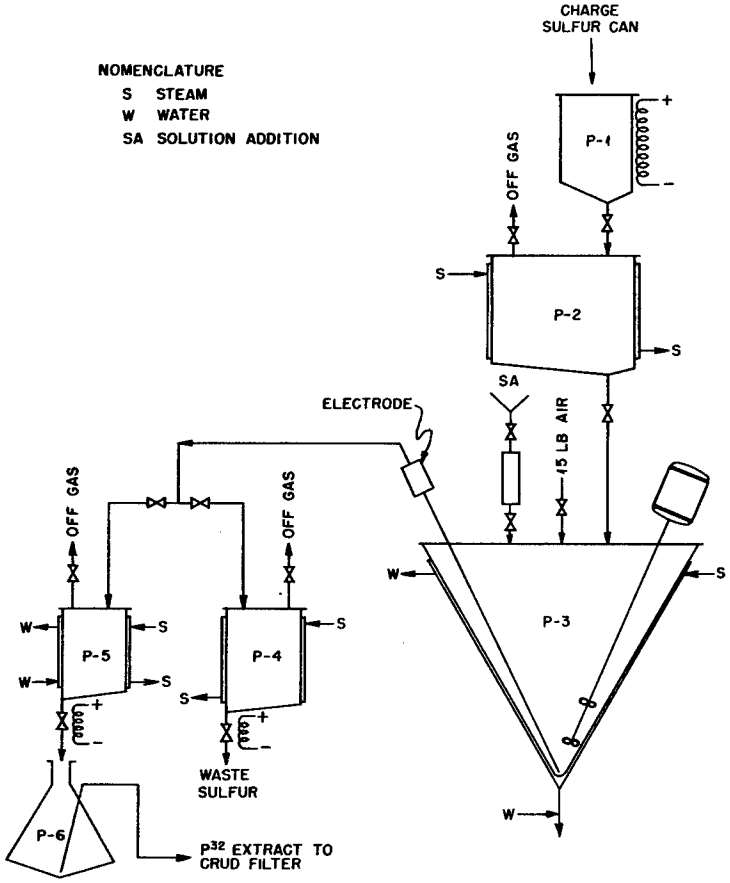

Fig. 6—Flow diagram of P^{32} extraction equipment (Cell 5).

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