GEPP-289

CALCIUM CHROMATE SYNTHESIS PROCESS

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Chemistry Laboratory Operation

April 25, 1977

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Prepared for the U. S. Energy
Research and Development Administration
Albuquerque Operations Office
Under Contract No. EY-76-C-04-0656

ABSTRACT

The calcium chromate synthesis process developed at General Electric Neutron Devices Department was investigated at a ten-pound yield level by producing forty-six batches of the product at this level. The effect of reaction temperature, recycling filtrate, recycling ammonia, and various washing procedures on product purity and yield was determined. Results from these investigations led to the development of a standard operating procedure for repeatedly producing calcium chromate to meet stated specifications. Five ten-pound batches were consecutively prepared to meet these specifications. These were blended and samples were analyzed.

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INTRODUCTION

The calcium chromate synthesis process developed at the General Electric Neutron Devices Department (GEND) during fiscal year 1975 involved synthesis studies on a laboratory level and a scale-up of the process to a ten-pound yield level. It was desirable to further evaluate this process at a ten-pound yield level using equipment comparable to the type of equipment that would be used on a production level.

This evaluation included a study of the effects of reaction temperature, ammonia recycling, filtrate recycling, and washing procedures on product yield and purity. Procedures were developed for repeatedly producing a product meeting the following specifications:

1. Minimum assay - 97% $CaCrO_4$ based on Cr(VI) titration.

2. Mole ratio Ca to Cr(VI) equal to or greater than one.

3. Total metal impurities as determined spectrographically and expressed as their most common oxides equal to or less than one percent.

4. Total hydroxyl ion content, expressed as calcium hydroxide equal to or less than one percent.

SYNTHESIS PROCESS AND EQUIPMENT

SYNTHESIS PROCESS

The synthesis process developed at GEND involves the addition of ammonium hydroxide to a chromic acid solution to form ammonium chromate and the subsequent addition of slaked lime to the ammonium chromate solution to form calcium chromate and ammonia. The reaction of ammonium hydroxide and chromic acid is an exothermic neutralization reaction and therefore the rate of addition of ammonium hydroxide can be used to control the reaction temperature. The completion of the neutralization process is indicated by a pH of 7.0 ± 0.2 when ammonium hydroxide addition is complete.

Toward the completion of the neutralization reaction, lime is added to water in the lime tank and the slaking reaction monitored by recording the temperature of the reaction. Upon reaction completion, the slaked lime is added to the ammonium chromate in the reaction tank. Figure 1 shows a typical temperature recording for these reactions. Calcium chromate forms immediately upon lime addition; however, the product is digested and pH monitored for approximately two hours. A constant pH value of 9.6 ± 0.2 indicates reaction completion. At the end of this time, the air pump is used to partially remove ammonia gas, a by-product of the process, from the reaction tank and exhaust it under water in the ammonia tank. The reaction tank contents are then throttled into the centrifugal filter where calcium chromate is separated from the filtrate reaction medium. The filtrate is directed to a holding tank for subsequent evaporation and disposal as solid waste material. The calcium chromate product is contained in a polyester bag inside the centrifugal filter. The product is removed from this bag and dried at approximately 120°C in stainless steel trays 3 cm deep.

PROCESS EQUIPMENT

Equipment used for this study was mounted on a 6- by 3-foot skid with a control panel for all instrumentation involved in the process. Basic pieces of equipment included three stainless steel tanks; a ten-gallon reaction tank, a five-gallon ammonia tank, and a two-gallon lime tank. The reaction tank was equipped with a variable speed, 1/2-hp mixer with connections suitable for work at reduced pressure.

A metering pump was used to transfer ammonium hydroxide from the ammonia tank into the reaction tank. This pump was of 316 stainless steel construction and had a maximum flow rate of 2667 mℓ/hr and a minimum flow rate of 267 mℓ/hr. A Moyno* pump constructed with a 316 stainless steel pump rotor and a Buna "N" elastomer pump stator was used for sampling reaction tank contents for pH measurements and for transferring filtrate from a holding tank for evaporation. An "oil-less" air pump was used to remove ammonia from the reaction tank and exhaust it under water to prevent its exhaustion into the atmosphere. A laboratory model centrifugal filter of stainless steel construction equipped with a fume-tight cover was used for separation of the final product from the reaction medium. This centrifugal had a basket speed of 1650 rpm.

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*Trademark, Robbins & Myers, Inc.

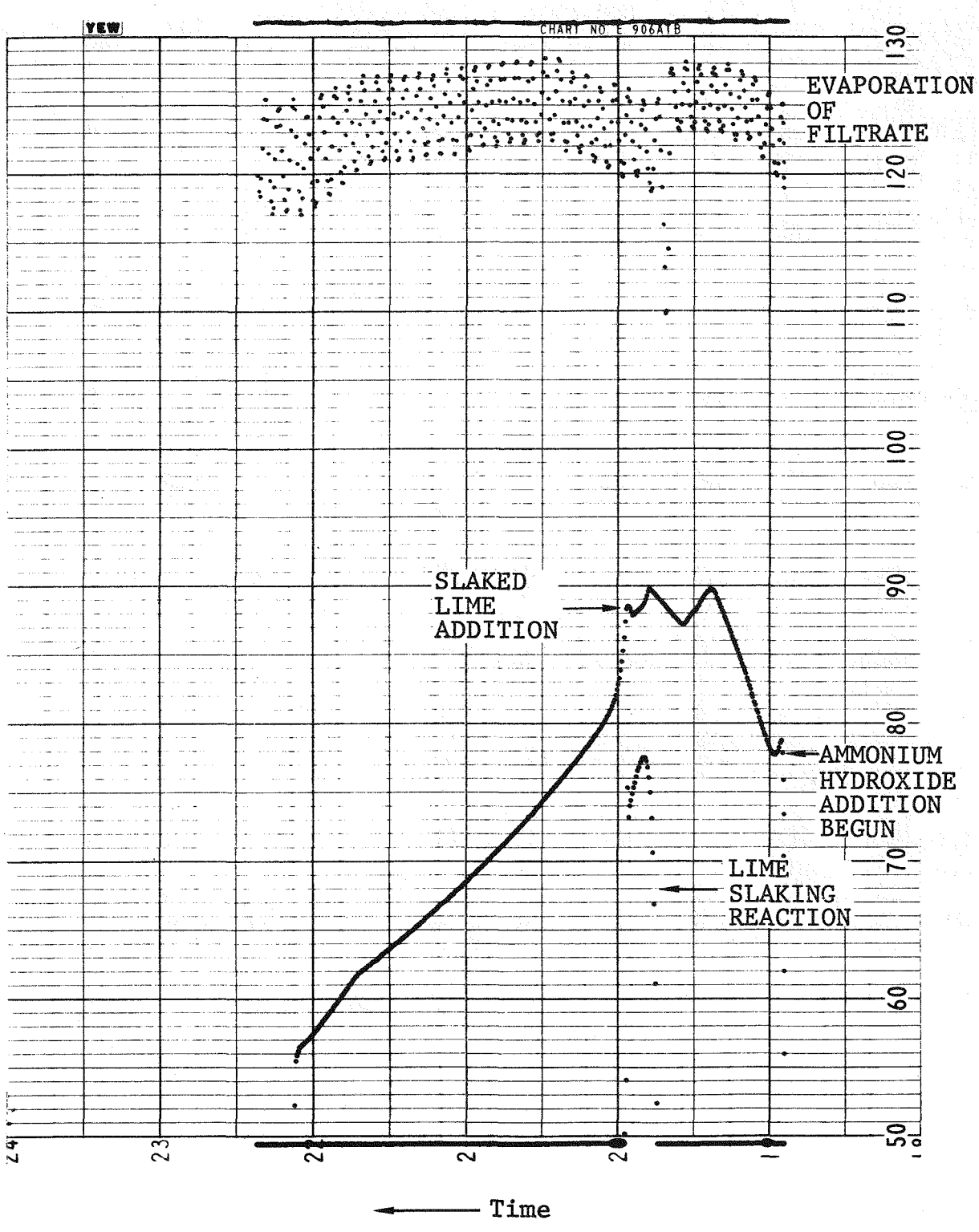

Figure 1. Process Temperature Recording

Instrumentation included a multipoint strip chart recorder which was used to record temperature in the reaction tank, lime tank, and drying oven. Temperature was measured by resistance bulbs constructed with nickel resistance winding encased in 316 stainless steel. These were installed in the reaction tank, lime tank, and oven. The rate of addition of ammonia to chromic acid in the reaction tank was controlled by a temperature controller which cycled the metering pump off and on to maintain a predetermined temperature. The pH of the reaction was monitored by continuous sampling of the reaction tank contents through a pH electrode assembly. This was a sealed Bakelite* compartment containing a pH measuring electrode and a silver-silver chloride nonflowing reference electrode. The pH was indicated by a pH-to-current converter installed in the control panel. Figure 2 shows process equipment and its arrangement on the skid.

EXPERIMENTAL RESULTS

Forty-six ten-pound batches of calcium chromate were prepared using the previously described process and equipment. Forty-two of these batches were analyzed to determine the purity of the product and to identify impurities present. Two samples were prepared early in the study and operational difficulties caused impurities which could be visibly identified. For this reason, further analysis was not pursued. The remaining two samples were lost, one by a spill and the other through equipment malfunction.

Unless specified otherwise, stoichiometric amounts of technical grade reagents were used in the preparation of all samples. The synthetic process involved the dissolution of 2844 g of chromium trioxide in 9.8 ℓ of the specified reaction medium, the controlled addition of approximately 3800 mℓ of ammonium hydroxide, and the further addition of 1595 g of calcium oxide slaked in 6 ℓ of water.

*Trademark, Union Carbide Corp.

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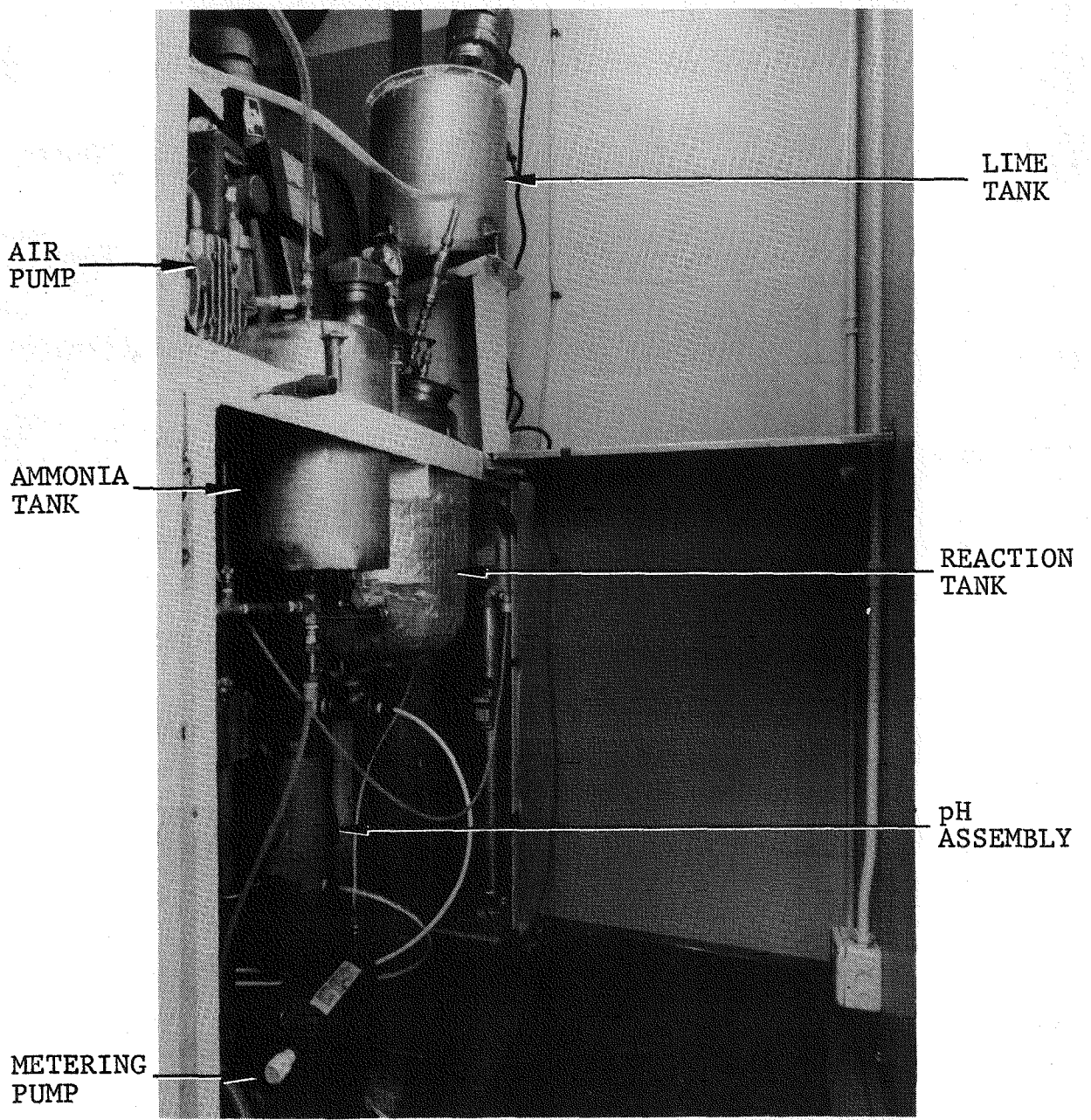

Figure 2. Process Equipment

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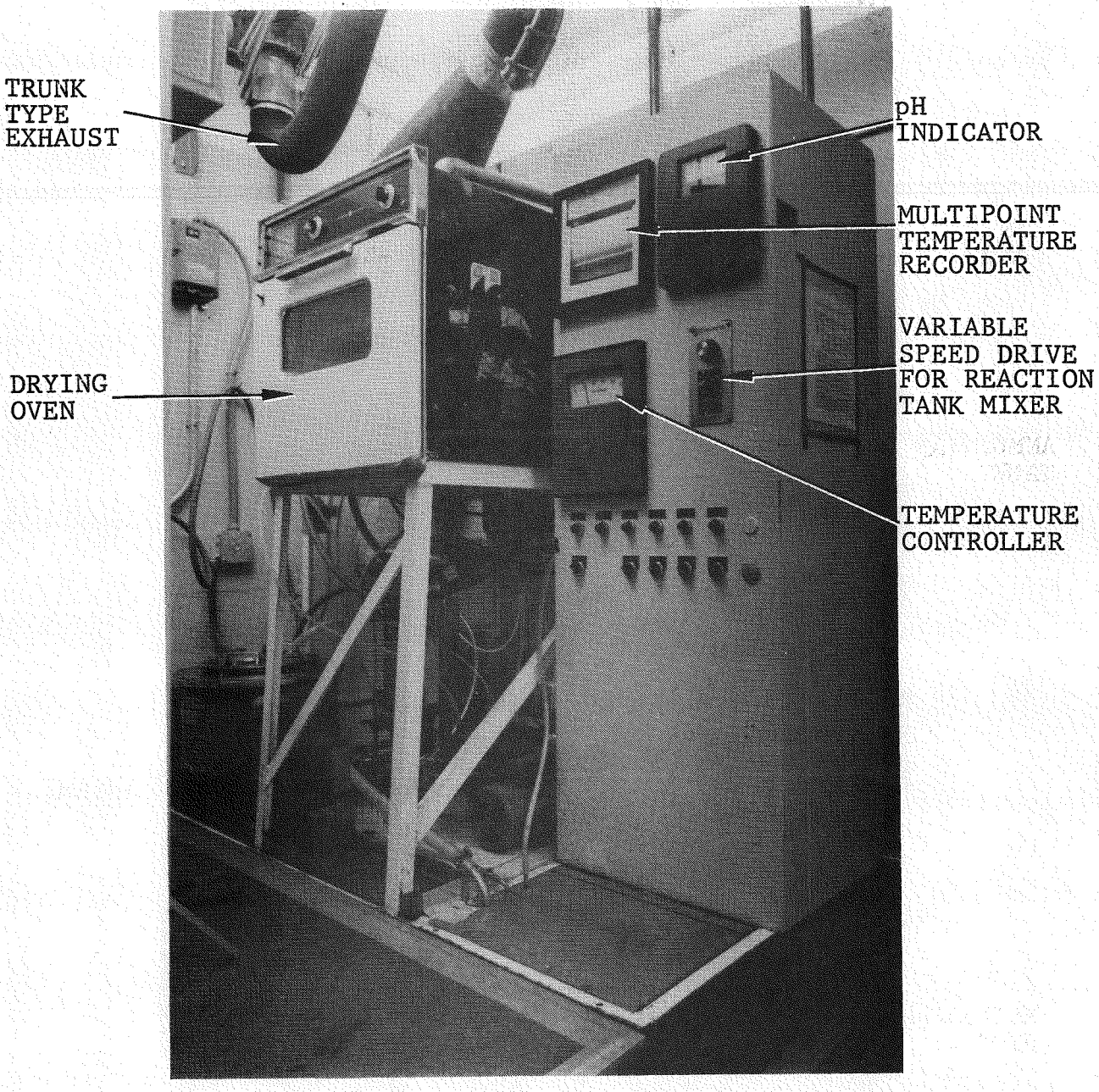

Figure 2 (Continued). Process Equipment

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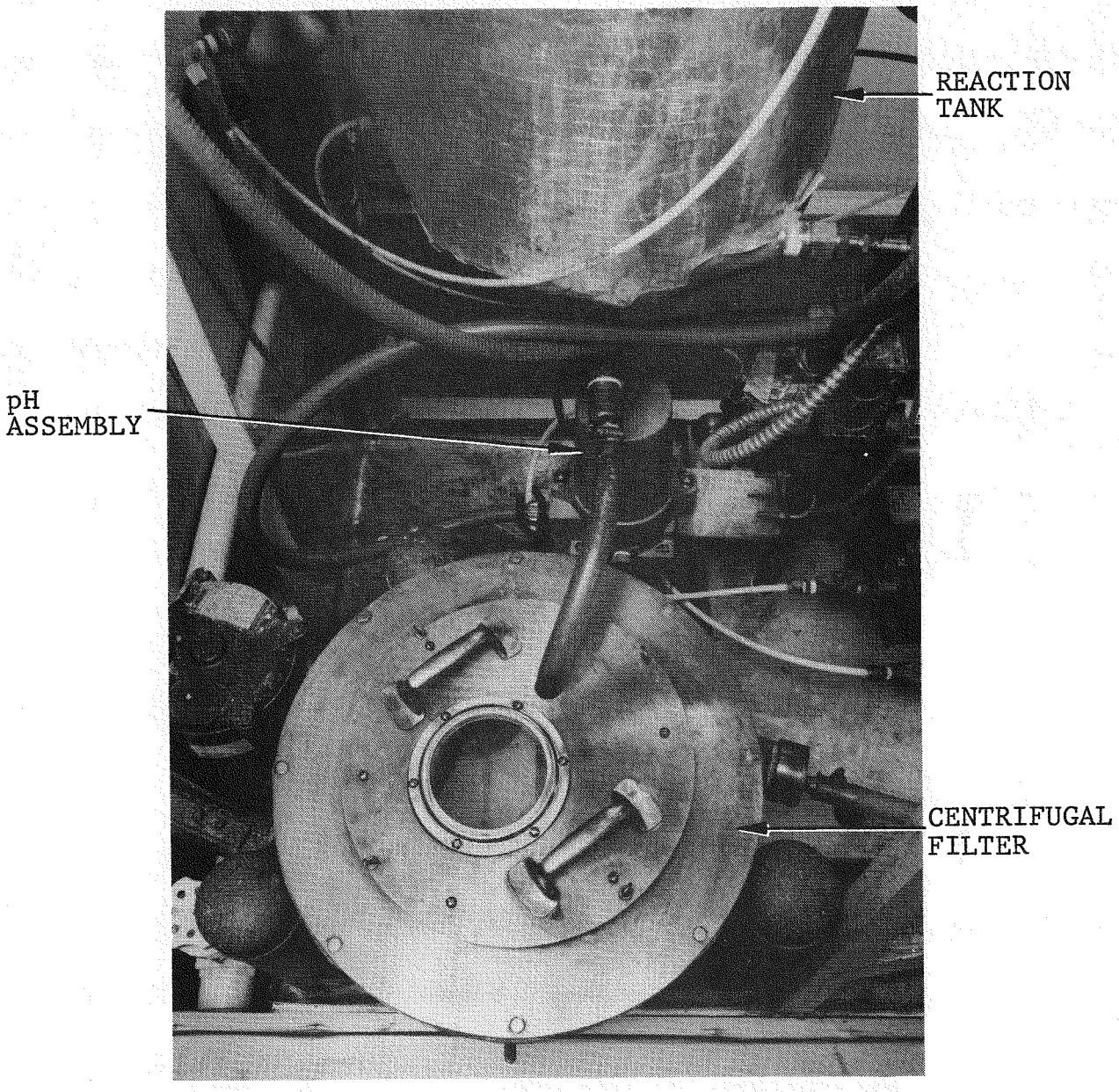

Figure 2 (Continued). Process Equipment

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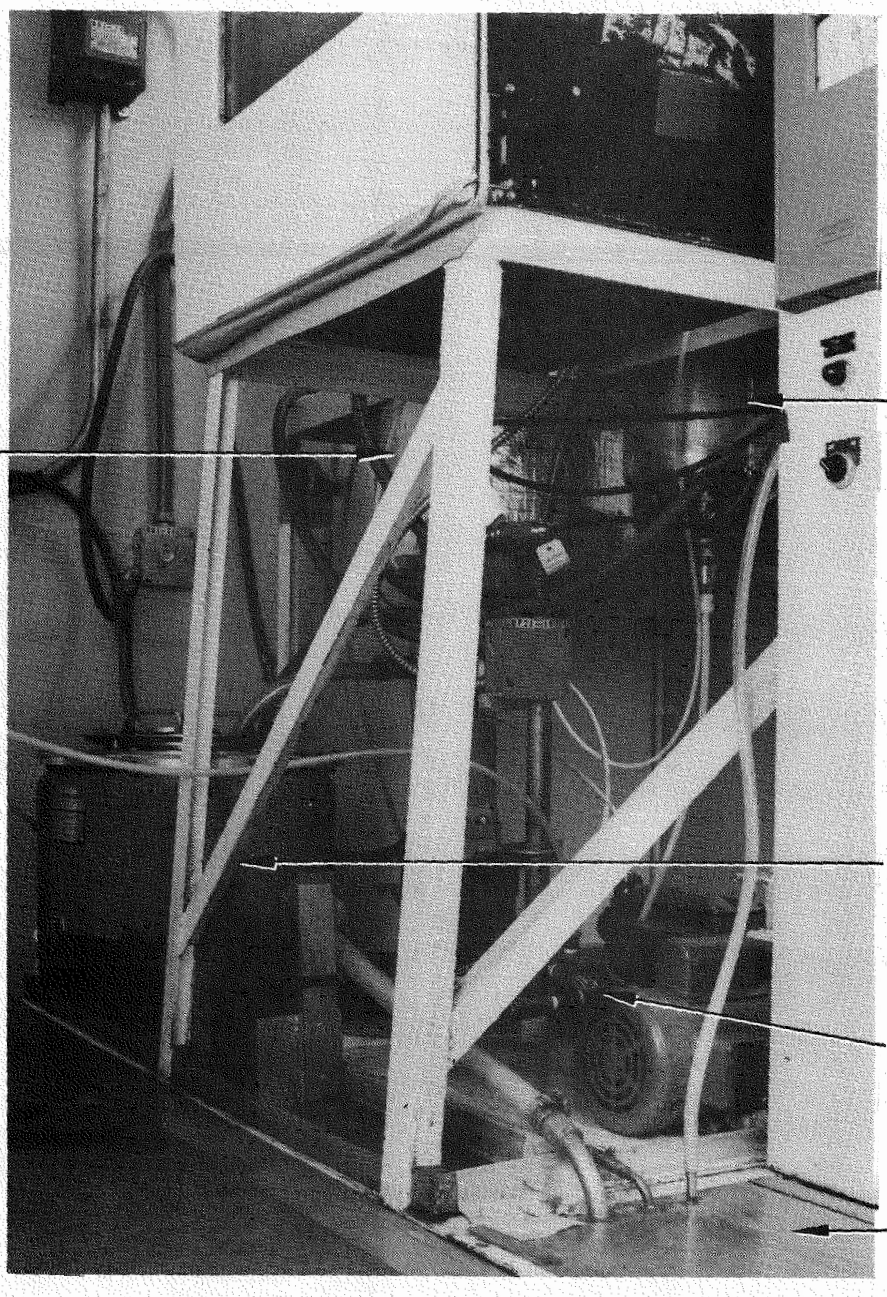

Figure 2 (Continued). Process Equipment

REACTION TEMPERATURE

The first process variable studied was reaction temperature. Previous studies had been at a 70°C reaction temperature, and it was desirable to determine if reaction temperature would affect product purity and yield. Samples prepared on a laboratory scale at temperatures below 70°C contained large amounts of calcium carbonate. For this reason, only temperatures of 70, 80 and 90°C were investigated. The temperature was controlled by the rate of addition of ammonium hydroxide. Results from these studies are included in Table 1.

Table 1. Effect of Reaction Temperature on Product Yield and Purity

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Batch No.	Reaction Temperature (°C)	$CaCrO_4$ (%)	Yield (%)	Ca (%)	$Ca(OH)_2$ (%)	$CO_3^=$ (%)	pH*
1	70	95.4	68.2	-	0.70	-	10.4
2	70	95.7	66.0	-	-	-	-
5	70	95.0	69.7	25.2	0.68	0.3	10.3
17	70	96.3	77.8	25.6	0.54	0.5	10.2
21	70	97.1	73.0	25.8	0.33	0.4	9.9
22	70	97.2	68.8	26.0	0.44	0.4	10.2
19	80	97.1	71.2	25.7	0.30	0.5	9.7
20	90	97.7	69.2	26.0	0.20	0.5	9.7
23	90	95.2**	60.8	26.9	0.48	0.5	10.1

*W. W. Welbon, R. J. Antepenko "Characterization of Calcium Chromate," GEND Technical Information Series Report, GEPP-211, May 1976.

**Moyno stator showed signs of deterioration from reaction with hot chromic acid. Stator was replaced after this run and procedure altered to prevent contact of Moyno stator with hot chromic acid.

Batches 1, 2 and 5 were prepared early in the study, and their low purity can probably be attributed to equipment and procedural difficulties. Analyses for Batches 17 through 22 seemed to indicate significantly higher purity for a 90°C reaction temperature compared with 70°C and 80°C reaction temperatures. Of importance also is the significantly lower hydroxide ion concentration for sample 20. This is probably due to the higher reaction temperature of 90°C.

With constant reagent amounts, the calcium hydroxide ion content should be determined by the degree of reaction completion. Since all batches were digested for the same length of time (2.0 hours), the reaction at higher temperatures should have been more complete for a given time period. Minimizing reaction time is important in considering efficient production schedules and also in preventing long periods of contact of calcium chromate with the reaction medium, thus increasing the solution of calcium chromate and lowering the yield of the product.

SLIGHT EXCESSES OF CALCIUM OXIDE AND CHROMIUM TRIOXIDE

Table 2 includes some analysis data for batches prepared using slight (~2%) excesses of either calcium oxide (lime) or chromium trioxide (chromic acid). Batches prepared early in the study were low in purity and had a green tint indicating the presence of chromium(III). It was felt this chromium(III) could be a decomposition product from excess ammonium chromate or chromic acid. Therefore, a slight excess of calcium oxide was used to drive the reaction to completion. However, this did not increase the purity of the product. While quantitative analysis for the carbonate ion had not been performed at this point in the study, the presence of carbonate was indicated in the product by effervescence upon dissolution in dilute hydrochloric acid. The concentration of hydroxide ion impurity in the final product was also high as shown in Batch 6. For these reasons it was

Table 2. Effect of Excess Reagent Amounts on Product Yield and Purity

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Batch No.	Reaction Temperature (°C)	Excess Reagent	$CaCrO_4^2$ (%)	Yield (%)	Ca (%)	$Ca(OH)_2$ (%)	$CO_3^=$ (%)	pH
6	70	Lime	95.9	75.2	25.2	0.63	-	10.4
7	70	Lime	95.4	69.8	-	-	-	-
8	80	Lime	95.4	72.3	-	-	-	-
9	80	Lime	93.9	72.6	-	-	-	-
11	70	Chromic Acid	96.2	70.3	25.5	0.22	0.8	9.8
16	70	Chromic Acid	96.0	77.7	25.5	0.13	0.3	9.5
12	80	Chromic Acid	96.1	71.6	25.6	0.35	0.5	9.9
15	80	Chromic Acid	96.3	72.8	25.3	0.41	0.3	9.9
13	90	Chromic Acid	96.5	76.0	25.2	0.22	0.5	9.7
14	90	Chromic Acid	96.9	70.7	25.3	0.20	0.5	9.6

felt that perhaps a slight excess of chromic acid would decrease the concentration of these impurities and thus increase the purity of the sample. Analyses for Batches 11 through 16, with excess chromic acid, show increased purity and a decrease in hydroxide ion concentration. However, the product was not meeting the purity specification of 97.0% calcium chromate. At this point, it was felt that stoichiometric reagent amounts should be further investigated since earlier results could have been due to equipment and procedural difficulties. Results from these studies are shown in Table 1 and have been previously discussed.

REACTION MEDIUM

Deionized Water and Distilled Water

While Batches 17 through 23 showed increased purity, the carbonate impurity concentration was still higher than desirable. The source of this impurity could have been due to carbonate impurities in the calcium oxide reagent, dissolved carbon dioxide in water used for the reaction, or carbon dioxide dissolved from the atmosphere during the reaction. Analysis of calcium oxide used for the reactions showed a carbonate ion concentration of 0.1%. To determine if the carbon dioxide impurity was associated with carbon dioxide dissolved in water, batches were prepared using a reaction medium of either boiled deionized (DI) water or distilled water. Results from these studies are shown in Table 3. A reaction medium of boiled DI water showed no significant increase in either product purity or decrease in carbonate ion concentration at any reaction temperature. Reactions in distilled water showed a significantly higher purity at a reaction temperature of 90°C as compared to 70°C reaction temperature. However, previous studies in DI water reaction medium had shown this same trend (Table 1).

No decrease in carbonate ion impurity concentration was noted in the distilled water reactions. Although distilled water did not appear to significantly affect the purity of the product, it was felt that due to the location of the process area in relation to the DI water circulation, distilled water should be used for further preparations since its purity was easier to control.

Distilled Water with Nitrogen Atmosphere

To investigate the other possible source of carbon dioxide, reactions were run in distilled water with a nitrogen atmosphere. Results are shown in Table 3. In all cases except for Batch 34, the carbonate ion concentration decreased significantly. Procedural difficulties in Batch 34 preparation probably account

Table 3. Effect of Reaction Medium on Product Purity and Yield

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Batch No.	Reaction Medium	Reaction Temperature (°C)	$CaCrO_4$ (%)	Yield (%)	Ca (%)	$Ca(OH)_2$ (%)	$CO_3^=$ (%)	pH
31	Distilled water	70	96.6	74.9	26.1	0.44	0.4	10.1
33	Distilled water	80	97.1	68.0	25.8	0.28	0.7	9.9
25	Distilled water	90	97.5	69.6	25.9	0.20	0.4	9.7
27	Distilled water	90	97.5	67.6	25.9	0.24	0.4	9.8
34	Distilled water, N_2	70	97.1	59.9	25.6	0.20	0.7	9.8
35	Distilled water, N_2	80	95.8	73.9	26.1	0.46	0.1	10.5
36	Distilled water, N_2	90	95.2	68.1	26.1	0.50	<0.01	10.8
38	Distilled water, N_2	90	96.8	65.5			0.1	
39	Distilled water, N_2	90	96.5	77.4	26.0	0.20	ND	9.7
30	Boiled DI water	70	96.8	66.3	26.2	0.41	0.4	10.2
32	Boiled DI water	80	97.0	70.1	26.5	0.22	0.7	9.8
24	Boiled DI water	90	97.0	70.9	26.0	0.28	0.4	9.9
26	Boiled DI water	90	97.1	68.5	25.9	0.26	0.4	9.8
22	Recycled filtrate	70	97.2	68.8	26.0	0.44	0.4	10.2
28	Recycled filtrate	70	96.7	79.0	26.1	0.35	0.3	9.9
29	Recycled filtrate	90	96.6	81.3	26.0	0.13	0.5	9.5
37	Recycled filtrate, N_2	70	97.0	76.9	25.8	0.22	~0.07	10.0

for the higher carbonate ion concentration. Although the carbonate ion concentration decreased significantly with use of a nitrogen atmosphere, the purity also significantly decreased at higher reaction temperatures. Mass balance calculations seemed to indicate an impurity other than carbonate or hydroxide ions.

Recycled Filtrate

The effect on product purity caused by using recycled filtrate as the reaction medium was studied at 70°C and 90°C reaction temperatures. Results are shown in Table 3. Reactions at 70°C showed no significant difference in product purity. However, the one reaction at 90°C showed a significant decrease in product purity. Since the filtrate must be heated to approximately 70°C in order to operate at a 90°C reaction temperature, large amounts of ammonia were evolved while chromium trioxide was being added to the reaction tank. For this reason, the reaction was not repeated. Batch 37 was prepared using recycled filtrate as the reaction medium and a nitrogen atmosphere. No significant change in product purity was noted although the carbonate ion concentration decreased significantly.

Recycling Ammonia

Since ammonium hydroxide is a starting material for the process and ammonia is a by-product of the process, the feasibility of recycling ammonia was investigated. A vacuum pump was used to remove ammonia from the reaction tank and exhaust it under water in the ammonia tank. After running this process for a period of 1 and 1.5 hours, the amount of ammonia recovered was 3.32 and 3.35% respectively. This amount was very small and it was felt that major changes would have to be made in equipment design to increase the amount. Therefore, the removal of the ammonia by-product was used only for the purpose of reducing the concentration of ammonia discharged through the exhaust system.

Washing

Washing procedures were studied first by comparing product purity and yield obtained by using three washing liquids. Results are shown in Table 4. These results indicated that none of the washing liquids investigated yielded a significantly purer product. Therefore, since operationally it was easiest to wash with room-temperature DI water, this was adopted as a standard procedure.

Table 4. Effect of Washing Liquid on Product Purity and Yield

Washing Liquid	Reaction Temperature (°C)	Average Purity (%)	Average Yield (%)
DI water (Room Temp)	70	96.6	71.2
DI water (~80°C)	70	96.9	73.2
DI water (Room Temp)	80	96.7	70.9
DI water (~80°C)	80	96.6	74.4
DI water (Room Temp)	90	97.0	75.9
DI water (~80°C)	90	97.2	69.5
Distilled water (Room Temp)	90	97.5	69.6

The procedure used to wash the centrifugal filter cake involved the addition of the washing liquid through the centrifugal port while the centrifugal was spinning at full speed. The uniformity of this washing procedure was investigated by sampling the filter cake at several different points before it was removed from the centrifugal. These samples were dried and analyzed for chromium(VI) to determine their purity. The results are shown in Table 5.

Sample B from both batches was of significantly lower purity. These samples were taken from a high portion of the filter cake and showed green coloration due to chromic oxide impurities. Since chromic oxide is denser than calcium chromate, assuming equal volumes for particles, the force on the chromic oxide would be greater than that on the calcium chromate. Therefore, chromic oxide would tend to migrate toward the top portion of the filter cake. Further washing would not decrease the concentration of this impurity since it is insoluble in both hot and cold water.

Table 5. Filter Cake Sample Purity

Batch No.	Sample No.	$CaCrO_4$ Percent
44	A	97.0
	B	96.4
	C	97.4
	D	97.2
46	A	97.2
	B	96.0
	C	96.9
	D	97.0

CONCLUSIONS

These studies indicated that the synthesis process could be adapted to ten-pound batches using the following standard experimental procedures:

1. Reaction temperature of 90°C.
2. Use of stoichiometric reagent amounts.
3. Digestion time of two hours with ammonia removal time of 15 minutes.
4. Use of DI water (room temperature) as washing liquid.

VERIFICATION

Using the experimentally derived procedures and standard equipment operating procedures, seven batches of calcium chromate were prepared to study the repeatability of the process. Analyses for these batches are shown in Table 6. Batch 41 fell below the purity specification of 97.0% calcium chromate by 0.2%. The hydroxide ion concentration was also higher for this batch than for the other batches.

Table 6. Process Reproducibility Data

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Batch No.	$CaCrO_4$ (%)	Yield (%)	Ca (%)	$Ca(OH)_2$ (%)	CO_2 (%)	pH	Metallic Impurities*					
							Al	Fe	K	Mg	Na	Si
40	97.3	74.5	26.0	-	-	-	-	-	-	-	-	-
41	96.8	73.3	25.9	0.33	-	10.0	-	-	-	-	-	-
42	97.4	73.2	25.8	0.22	0.4	10.0	0.06	0.03	0.001	0.2	0.004	0.4
43	97.6	75.7	25.8	0.17	0.4	10.2	0.06	0.03	0.002	0.2	0.004	0.4
44	97.8	75.9	25.8	0.28	0.4	10.1	0.06	0.03	0.001	0.2	0.004	0.4
45	97.2	73.3	25.4	0.26	0.4	10.0	0.06	0.03	0.002	0.3	0.004	0.2
46	97.8	74.2	25.6	0.24	0.3	10.0	0.06	0.03	0.003	0.3	0.003	0.2

*Reported as most common oxides.

Batches 42 through 46 were dried at 110°C then ball milled and dried again at 110°C. These batches were blended and a core sample taken for analysis. The particle size distribution of this sample was determined on the Sedigraph 5000. The distribution curve is shown in Figure 3. Surface area of the sample was determined on a Monosorb* Surface Area Analyzer using a modified Brunauer-Emmett-Teller method. Results indicated a surface area of 4.7 m^2/g.

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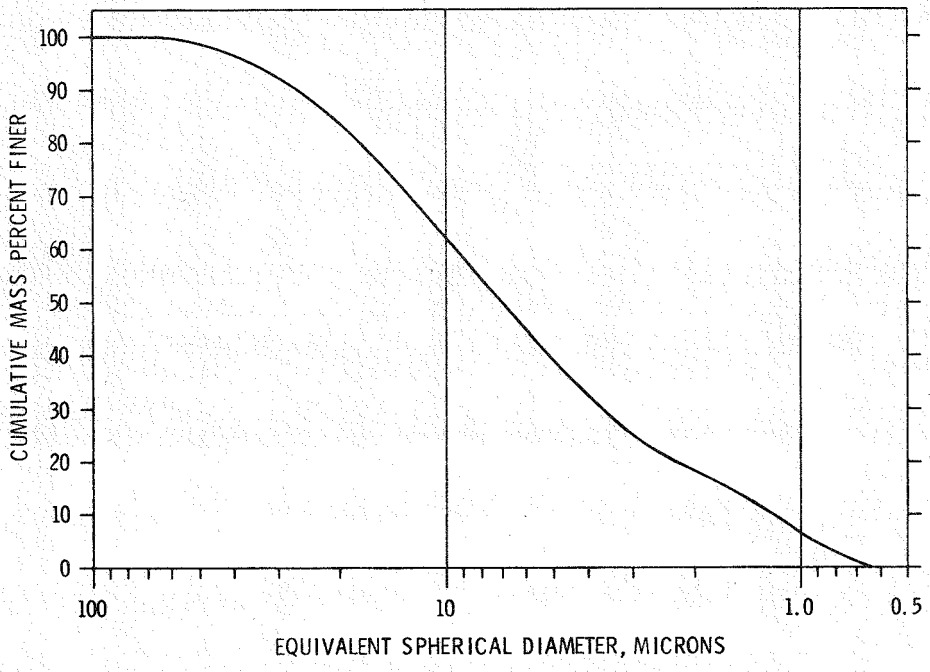

Figure 3. Particle Size Distribution-
Blend of Batches 42 Through 46

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ACKNOWLEDGMENT

The author wishes to acknowledge the assistance of the following GEND Chemistry Laboratory personnel: M. Brown, in product synthesis and C. P. Lofton, in coordinating chemical analyses for the products.

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