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CALCIUM CHROMATE PROCESS RELATED INVESTIGATIONS

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August 29 , 1979

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Prepared for the
U. S. Department of Energy
Albuquerque Operations Office
Under Contract No. DE-AC04-76DP00656

ABSTRACT

A pilot plant for production of calcium chromate has been scaled up to a small production facility at the General Electric Neutron Devices Department. In preparation for this scale-up, the process and final product were studied in order to evaluate problems not considered previously. The variables and processes studied included: (1) the determination of optimum drying temperature and time for product analysis; (2) the effect of the grade of lime used as the precipitating agent on the purity of the calcium chromate ; (3) product purity when calcium chromate is precipitated by the addition of ammonium chromate to slaked lime; (4) the reagents best suited for cleaning calcium chromate spills; (5) methods for determining hydroxide ion concentration in calcium chromate.

Conclusions from this study included the following. The optimum drying time for the product before analysis is four hours at 600°C. Gases evolved at various temperatures during the drying process were carbon dioxide and water vapor. Technical grade lime produced calcium chromate of the highest purity. Both nitric and acetic acids were efficient dissolvers of calcium chromate spills. Direct titration of hydroxide ion with sulfuric acid gave an average recovery of 93% for samples spiked with calcium hydroxide.

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INTRODUCTION

The process developed at the General Electric Neutron Devices Department (GEND) for the synthesis of calcium chromate used in thermal batteries involves the neutralization of chromic acid with ammonium hydroxide and the subsequent addition of calcium oxide for precipitation of calcium chromate.[1] This pilot plant process has been scaled up to a production facility that is currently in operation.[2] In preparation for this scale-up, the process and final product were further studied in order to evaluate variables and process related problems not considered previously.[3] These variables included the following:

1. Determination of the optimum drying time and temperature needed for the product before analysis, including an analysis of the gases evolved at various temperatures during the drying time.
2. Effect of the grade of lime used as the precipitating agent on the purity of the calcium chromate.
3. Determination of product purity when calcium chromate is precipitated by the addition of ammonium chromate to slaked lime.
4. Evaluation of reagents that could be used for removing calcium chromate spills in the process area.
5. Evaluation of the present method used for determining hydroxide ion concentration in calcium chromate and the investigation of an alternative method.

DRYING TEMPERATURE INVESTIGATIONS

CALCIUM CHROMATE ANALYSIS AS A FUNCTION OF DRYING TIME AND TEMPERATURE

GEND calcium chromate from the pilot plant facility is routinely dried on trays in an oven at 140°C for 16 hours before grinding and packaging. Calcium chromate from the production facility is routinely dried in a rotary vacuum drier at 150°C for a minimum of four hours before grinding and packaging. Commerical, as well as GEND calcium chromate, has routinely been further dried at 400°C for 4 hours before analysis or use in the thermal battery.

In order to optimize the latter drying time and temperature conditions for GEND calcium chromate, drying temperatures of 200, 400, 500, 600, 650, and 700°C for periods of two, four, six, and eight hours were investigated.

This investigation was done in two phases. Phase one involved drying temperatures of 200, 400, 500, and 600°C with times of two, four, six, and eight hours. The calcium chromate sample designated No. 194 was used for this phase. This sample had been prepared, dried, and ground using the standard operating procedures described previously.[3]

Eight 20-gram samples of calcium chromate were placed in a muffle furnace at 200°C. Two samples were removed at the end of periods of two, four, six, and eight hours. The percent weight loss and the percent of Cr(VI) were determined for each sample. Results are reported in Table 1. The sample was dried for 8 hours and further analyzed for the percent of calcium, carbon dioxide, hydroxide, metallic impurities and for surface area. The sample dried for 4 hours at 400°C was also further analyzed since, at that time, this was the routine drying process before analysis or use in the thermal battery. The above procedure was repeated for drying temperatures of 400, 500, and 600°C. All results are reported in Table 2.

The second phase of the study involved drying temperatures of 600, 650, and 700°C for periods of two, four, six, and eight hours. Calcium chromate sample No. 254 was used for this work. This sample was also prepared, dried, and ground using standard operating procedures described previously.[3] The experimental process described for Phase 1 was also followed for Phase 2.

Results are reported in Tables 3 and 4.

The first phase of the drying time/temperature investigation indicated that samples reached a constant weight loss after drying for 4 hours at 600°C. The percent purity increased for samples dried according to this procedure compared with samples dried according to the routine procedure of 4 hours at 400°C. Table 2 shows that the carbonate ion decreased after drying at 600°C for 8 hours. This is due to the decomposition of calcium carbonate to calcium oxide. In

Table 1. Weight Loss and % Purity as a Function of Drying Time and Temperature

	TEMPERATURE							
	$200^{\circ}C$		$400^{\circ}C$		$500^{\circ}C$		$600^{\circ}C$	
TIME (hrs.)	WT.LOSS(%)	PURITY(%)	WT.LOSS(%)	PURITY(%)	WT.LOSS(%)	PURITY(%)	WT.LOSS(%)	PURITY(%)
2	0.11	96.1	1.18	97.4	1.82	98.2	2.09	98.4
4	0.15	96.2	1.51	97.5	1.97	98.4	2.15	98.5
6	0.19	96.4	1.66	97.4	2.02	98.2	2.16	98.6
8	0.24	96.1	1.70	97.6	2.04	98.5	2.15	98.2

Table 2. $CaCrO_4$ Analyses as a Function of Drying Time and Temperature

DRYING TEMP.($^{\circ}C$)	DRYING TIME(hrs.)	%$CaCrO_4$	%Ca	%CO_2	%OH^-	pH	% METALLIC IMPURITIES				SURFACE AREA (M^2/g)
							Si	Mg	Al	Fe	
200	8	96.1	25.6	<0.01	0.09	9.9	0.2	0.1	0.05	0.03	7.3
400	4	97.7	25.5	<0.01	0.09	9.9	0.2	0.1	0.05	0.02	4.1
400	8	97.5	26.0	0.06	0.10	10.0	0.2	0.1	0.05	0.03	2.7
500	8	98.3	26.2	0.06	0.11	10.0	0.2	0.2	0.04	0.04	2.8
600	8	98.5	26.2	0.04	0.16	10.2	0.1	0.2	0.03	0.02	1.9

Table 3. Weight Loss and % Purity as a Function of Drying Time and Temperature

TIME (hrs.)	TEMPERATURE					
	600°C		650°C		700°C	
	WT.LOSS(%)	PURITY(%)	WT.LOSS(%)	PURITY(%)	WT.LOSS(%)	PURITY(%)
2	1.95	97.9	2.19	97.8	2.38	98.2
4	2.06	97.8	2.38	98.0	2.49	98.2
6	2.11	98.1	2.41	98.2	2.54	98.4
8	2.11	97.8	2.43	98.1	2.57	97.8

Table 4. $CaCrO_4$ Analyses as a Function of Drying Time and Temperature

DRYING TEMP.(°C)	DRYING TIME(hrs.)	$\%CaCrO_4$	%Ca	$\%CO_2$	$\%OH^-$	pH	% METALLIC IMPURITIES				SURFACE AREA (M^2/g)
							Si	Mg	Al	Fe	
400	4	97.4	24.3	0.10	0.10	9.9	0.4	0.16	0.02	0.02	3.4
600	4	97.8	24.5	0.07	0.20	10.2	0.4	0.16	0.02	0.02	1.8
600	8	97.8	24.5	0.09	0.18	10.4	0.4	0.16	0.02	0.02	1.9
650	8	98.1	24.6	0.01	0.35	10.5	0.4	0.15	0.02	0.02	1.5
700	8	97.8	24.7	0.01	0.36	10.5	0.4	0.14	0.02	0.02	0.8

*Sample No. 254

solution this would be converted to calcium hydroxide thus increasing the concentration of this ion. Surface area also decreased with increased drying time and temperature.

The second phase of the study involved higher drying temperatures using another sample of calcium chromate. This sample had a percent purity of 97.4 percent after drying at 400°C for 4 hours as compared to a percent purity of 97.7 percent with the same drying condition for the sample used in Phase 1. The drying temperature work was repeated for 600°C with the weight loss being approximately the same as that determined in Phase 1 for the 600°C drying. The change in percent purity was not significant with increased drying time at this temperature. Weight loss continued to increase with increased drying temperature. Temperatures above 700°C were not investigated since data indicated product decomposition began in this range. The highest purity was obtained for a drying temperature at 700°C for 6 hours. The concentration of carbon dioxide decreased with drying time and temperature, becoming constant after drying at 650°C for 8 hours. The hydroxide ion concentration also increased as the carbonate ion concentration decreased, indicating the conversion of the calcium oxide to hydroxide in solution. Surface area continued to decrease with increased drying time and temperature. As a result of this work, the drying procedure for GEND calcium chromate was changed to 4 hours at 600°C rather than 4 hours at 400°C. All samples of GEND calcium chromate used for analysis are also dried in this manner.[4]

THERMAL DESORPTION ANALYSIS OF $CaCrO_4$

In order to determine the gases evolved during the drying cycle, several samples of $CaCrO_4$ were characterized by thermal desportion.[5] (This involves ramp heating a sample at a linear rate under vacuum.) The gases evolved are scanned with a mass spectrometer at intervals during the thermal ramp and plots made of gas evolution rate versus temperature for the evolved gases.

The sample container consists of a 17- by 5-mm quartz test tube with a molybdenum wire support. This test tube with 40 to 50 mg of $CaCrO_4$ is placed in a quartz heating tube. A vacuum of 10^{-7} torr is attained with a cyro-trapped mercury diffusion pump that is conductance limited. A schematic for the instrumentation is shown in Figure 1. Heat is applied to the quartz tube by an external quartz lamp parabolic heater. Prior to ramp heating, the walls of

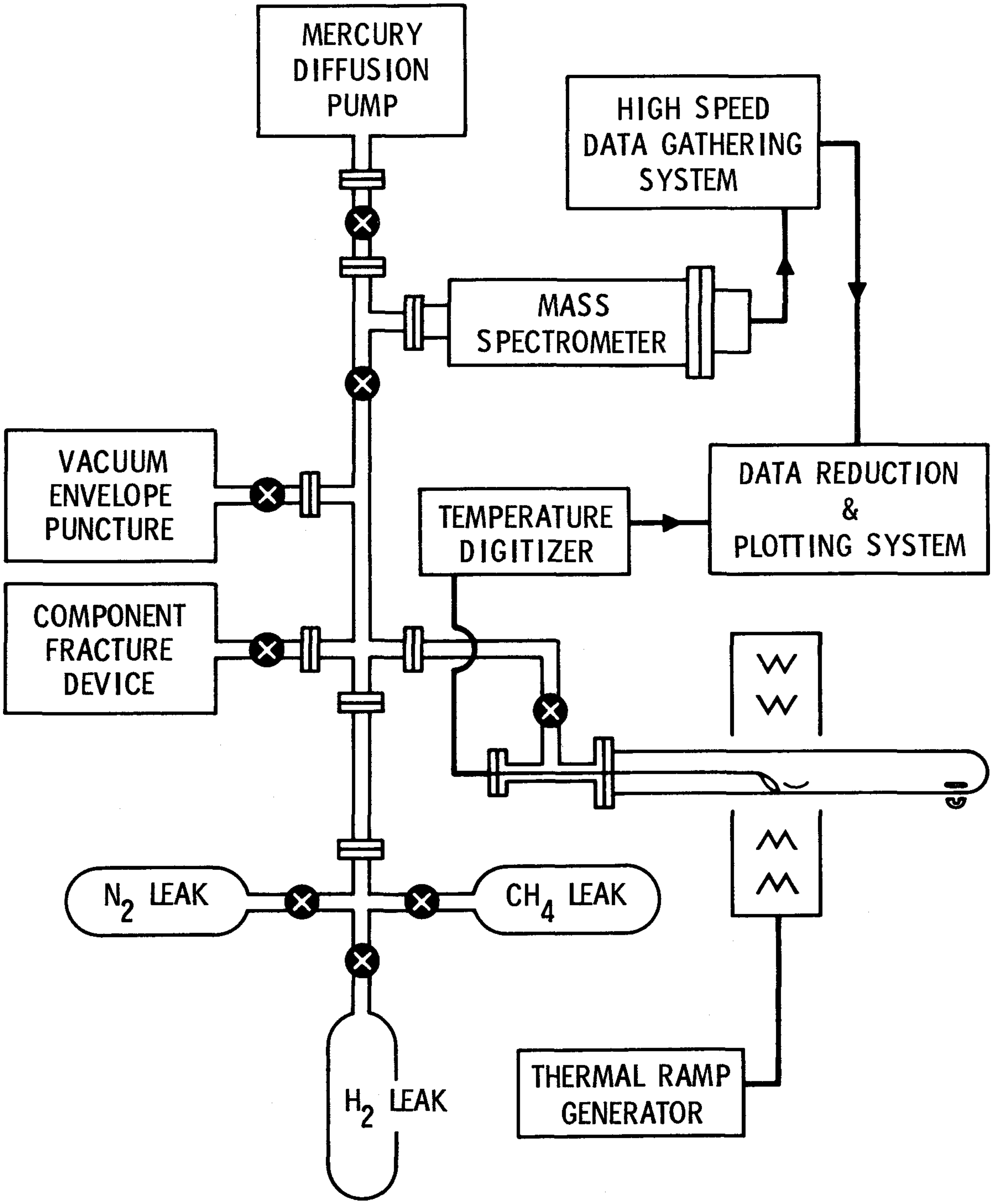

Figure 1. Thermal Desorption Analysis Equipment, Schematic

the hot zone are degassed while the sample remains in a cool portion of quartz heating tube. After cool down, the sample test tube container is moved to the ramping zone using a magnetic actuator and without breaking vacuum. Heat is applied to the sample by gradually increasing the voltage to the parabolic heater in such a manner that the temperature rises at a linear rate of 5°C/minute. During the ramp heating process, an internal platinum-platinum/10% rhodium thermocouple monitors the temperature. This temperature is converted to a binary count decimal signal, which is fed to a Hewlett-Packard HP9825A mini-computer. A quadrupole mass spectrometer monitors the gases as they are pumped away and feeds this data to a Hewlett-Packard computer. Data is then transferred to a dedicated plotter where evolution rate, in relation to temperature, is plotted for each mass detected. Each data point is corrected for background by running a "blank" of the sample test tube and wire support only. The mass spectrometer is calibrated by measuring the response for calibrated leaks in the on and off position. Quantitative gas evolution data is obtained by integrating under the evolution rate versus time curve for each mass detected.

Five samples of calcium chromate were analyzed by thermal desorption. The sample sources are shown in Table 5.

Table 5. Sources of Samples Analyzed by Thermal Desorption

Sample Designation	Source of Sample
26-1	GEND production facility not vacuum dried
27-1	GEND production facility not vacuum dried
243	GEND pilot plant facility
Blend 12	GEND pilot plant facility
Var-Lac-Oid 2	Var-Lac-Oid
929	GEND production facility not vacuum dried
943	GEND production facility vacuum dried

The major gases detected for these samples were water, carbon dioxide and oxygen. Figures A-1 through A-23 show plots of the rate of evolution of these species with the temperature of each sample.

Figures A-1 through A-7 show the rate of evolution of oxygen (mass 32) which is produced by the decomposition of calcium chromate. The rate of evolution for all GEND samples was very similar. However, oxygen evolution for the Var-Lac-Oid-2 sample appears to begin a a lower temperature than the GEND samples.

One source of the evolved water (mass 18) plotted in Figures A-9 through A-15 is from the decomposition of calcium hydroxide impurity in calcium chromate. Figure A-8 shows a plot of the rate of evolution of water from the decomposition of calcium hydroxide to calcium oxide. This water is in the range of 500°C. Sample 26-1 (Figure A-9) had water evolved mainly in this region. However, all other samples had water evolved in this region as well as at higher temperatures. There are four known hydrates of calcium chromate: a hemihydrate, a monohydrate and two different dihydrates. All four of these hydrates lose their water of hydration at temperatures below 200°C. Mylius and von Wrochem[6] report that the heating of calcium chromate hydrates can lead to pseudomorphism, producing materials such as $CaCrO_4 \cdot 1/4\ H_2O$. The evolution of water from these materials then takes place at much higher temperatures, since it is more tightly bound than in the normal hydrates. This type of bound water appears to be present in all samples except 26-1. Var-Lac-Oid-2 was the only sample that lost a substantial amount of water below 300°C. Data for the GEND samples agree with previous work with GEND calcium chromate in which this bound water was studied by thermograometry, evolved gas analysis and nuclear magnetic resonance methods.[7]

Samples 26-1, 27-1, 929, and 943 were dried differently than samples 243 and blend 12. Samples 26-1, 27-1, 929, and 943 were from the production facility and were dried in a rotary dryer at 150°C. Samples 243 and blend 12 were from the pilot facility and were dried on trays in an oven at 150°C. Sample 943 was dried in the rotary dryer but with vacuum. No information was available on the drying process for Var-Lac-Oid-2. Samples 26-1 and 27-1 had a lower purity than samples 929 and 943 (Table 16) and sample 26-1 was dried at 150°C for 8 hours as compared to 5 hours in the range of 150 to 165°C for the other samples. Samples 929 and 943 were dried under the same conditions except that vacuum (25 in. Hg) was used for sample 943. There was no significant difference in the rate of evolution versus temperature for these latter two samples.

The other major gas evolved was carbon dioxide (mass 44) from the decomposition of calcium carbonate impurity. Plots for the evolution of this gas, with temperature, are shown in Figures A-13 through A-17. Figure A-12 shows a plot of the rate of evolution of carbon dioxide from calcium carbonate with increasing temperature. This evolution is in the range of 900°C.

Sample 26-1 has a rather large amount of carbon dioxide released below this temperature. All other samples show evolution in the 800° to 900°C range.

Table 6 gives a comparison of analytical data from wet chemical analyses and thermal desorption. The percentage of carbon dioxide determined by thermal desorption was lower than that determined by the wet chemical method in all cases but one. This is probably because all the CO_2 is not evolved during the heating ramp for thermal desorption. Holding the sample in the 800° to 950°C range for a longer time period should give better quantitative results. The percent of water obtained by thermal desorption cannot be

Table 6. Comparison of $CaCrO_4$ Analysis by Thermal Desorption and Wet Chemical Analysis

Sample No.	Thermal Desorption*		Wet Chemical Analysis			
	CO_2 (%)	H_2O (%)	$CaCrO_4$ (%)	OH^- (%)	CO_2 (%)	Weight Loss to 600°C (%)
26-1	0.5	1.3	82.3	7.43	0.63	0.94
27-1	0.2	0.5	94.7	1.47	0.47	0.96
Blend 12	0.1	2.1	97.6	0.12	0.02	2.48
243	0.4	2.1	96.6	0.19	0.64	2.26
Var-Lac-Oid-2	0.4	2.1	NA	NA	NA	NA
929	0.2	2.9	97.1	0.22	0.46	2.92
943	0.1	1.7	97.7	0.15	0.29	2.60

*Temperature ramp to 950°C

compared directly with the percent weight loss to 600°C since a significant amount of water is evolved above 600°C and also some carbon dioxide is evolved in the 600°C range. The percent weight loss at 600°C was calculated after the sample was held at this temperature for 4 hours, while the thermal desorption data was obtained with a temperature range of 5°C/minute.

EFFECT OF GRADE OF LIME ON $CaCrO_4$ PURITY

Calcium oxide or quicklime is used as the precipitating agent for calcium chromate. Two of the impurities, carbonate and hydroxide ions, seen in largest concentrations in calcium chromate, come largely from this reagent.

Four grades of calcium oxide were used to prepare calcium chromate samples by standard operating procedures[1] in order to determine the effect of the purity of the lime on the final product. Each lime sample was analyzed before use and results are shown in Table 7. Total calcium oxide is a determination of the total calcium in the sample reported as calcium oxide. Available calcium oxide determines water soluble calcium compounds only, i.e., calcium oxide and calcium hydroxide. The weight loss at 600°C indicates some absorbed moisture and water evolved from the decomposition of calcium hydroxide.

Table 7. Lime Analyses

GRADE	TOTAL CaO	AVAILABLE CaO	%CO_2	%WT.LOSS AT 600°C (4 hrs.)	% METALLIC IMPURITIES					
					K	MgO	Si	Al	Fe	Na
Certified	93.6	91.7	1.23	1.60	-	0.5	0.4	0.1	0.07	0.01
Technical	90.2	88.9	0.63	7.51	-	0.5	0.3	0.08	0.06	0.1
Purified	85.8	83.5	0.33	1.70	0.08	1.4	∿1	∿0.05	0.2	0.03
Cerac Pure (1)*	96.3	94.2	0.58	0.58	-	0.41	0.2	0.07	0.06	-
Cerac Pure (2)	96.5	94.1	0.44	0.21	-	0.83	0.3	0.10	0.05	-

*X-ray emission showed Zr, Th, Ca, Ti.

XRD showed ThO_2, ZrO_2 and probably $.85\ ZrO_2 - .15\ CaO$.

The Cerac Pure-2 lime had the highest percent of total calcium oxide and available calcium oxide. The certified grade was next highest in the percent of total calcium oxide, but was highest in the percent of carbon dioxide.

Analytical data for samples prepared with these grades of lime are given in Table 8. The highest purity samples were obtained with technical grade and Cerac Pure-2 lime. The carbon dioxide and hydroxide ion impurities, as well as the metallic impurities, were comparable for these samples. The technical grade lime used for these experiments was the same as that routinely used for production. The samples prepared with certified lime contained the highest percentage of carbon dioxide. This grade of lime also contained the highest percentage of carbon dioxide. The samples prepared with purified lime contained a high percentage of silicon that was also present in a high concentration in the lime.

Table 8. Analyses of $CaCrO_4$ Produced With Different Grades of Lime

						WT. LOSS		% METALLIC IMPURITIES			
SAMPLE No.	LIME GRADE	$\%CaCrO_4$	%Ca	$\%CO_2$	$\%OH^-$	400°C	600°C	Si	Mg	Al	Fe
243	Certified	96.6	25.9	0.64	0.19	1.61	0.65	0.2	0.2	0.01	0.02
244	Certified	96.3	25.6	0.70	0.19	1.78	0.73	0.2	0.3	0.01	0.02
245	Technical	97.5	25.7	0.41	0.18	1.38	1.03	0.1	0.2	0.01	0.01
246	Technical	97.3	25.6	0.36	0.15	1.48	0.74	0.2	0.2	0.01	0.03
247	Purified	94.7	25.2	0.25	0.16	1.44	0.86	1.0	0.3	0.01	0.04
248	Purified	94.6	25.2	0.23	0.18	1.47	0.96	1.0	0.3	0.01	0.04
287	Cerac Pure(2)	97.0	25.5	0.27	0.18	1.67	0.72	0.2	0.3	0.04	0.03
288	Cerac Pure(2)	97.3	25.5	0.54	0.14	1.87	0.61	0.1	0.1	0.03	0.02

XRD - only anhydrous $CaCrO_4$ in 245, 246, 247, 248, 287, 288
detect $CaCO_3$ in 243, 244

This work showed that the purity of calcium chromate produced was directly related to the purity of the lime used in the preparation. Insoluble impurities in the lime, such as carbonates and silicon compounds, will also appear in calcium chromate. Concentration of the impurities is directly related to concentration in the lime that is used for preparation of the samples.

DETERMINATION OF PURITY OF PRODUCT PREPARED BY ADDITION OF AMMONIUM CHROMATE TO SLAKED LIME

The formation of a precipitate may be described generally as the following process:[8]

Ions in the solution (size 10^{-8}cm)	$\longrightarrow$	colloidal particles (size 10^{-7} to 10^{-4} cm)	$\longrightarrow$	precipitate (size $> 10^{-4}$ cm)

The standard GEND operating procedure for production of calcium chromate involves the controlled addition of slaked lime to an ammonium chromate solution. The precipitation process thus involves the formation of calcium chromate in the ammonium chromate solution as lime is gradually added. Due to the solubility of calcium chromate, the first ions formed would be in solution; but as the concentration of calcium chromate is increased, these ions would grow as described above, producing the calcium chromate precipitate. In this precipitation process, the concentration of calcium chromate nuclei exceeds that of slaked lime during the greater part of the precipitation process.

The other possibility for the precipitation process involves the addition of the ammonium chromate to the slaked lime. In this case, particles of calcium hydroxide exist that must be converted to calcium chromate nuclei. Since the calcium hydroxide particles are in excess as ammonium chromate is added, the formation of calcium chromate could require a longer time period.

Three samples of calcium chromate were prepared using the latter precipitation sequence with the same digestion time and temperature as for the standard procedure. These samples were analyzed to determine if the latter precipitation process affected the product purity. Results are reported in Table 9.

Table 9. Analyses for $CaCrO_4$ Prepared by Addition of $(NH)_2CrO_4$ to $Ca(OH)_2$

SAMPLE No.	$\%CaCrO_4$	%Ca	$\%CO_2$	$\%OH^-$	pH	SURFACE AREA (M^2/g)	% WT.LOSS AT 600°C	MEAN PARTICLE SIZE (μ)	Mg	Si	Al	Fe
1	96.5	26.4	0.24	0.91	11.0	1.3	2.92	10.2	0.15	0.3	0.03	0.03
2	96.8	26.4	0.14	0.92	11.0	1.1	2.99	11.0	0.13	0.2	0.04	0.03
3	96.1	25.8	0.26	0.94	11.1	1.4	3.09	14.0	0.14	0.1	0.04	0.03

The product purity for these samples was lower than that for samples prepared using the standard precipitation process. The major impurity was hydroxide ion which would seem to indicate incompleteness of the calcium chromate forming reaction at the digestion time and temperature used. With a longer digestion time or higher digestion temperature, the hydroxide ion concentration would probably decrease to levels normally seen with the standard precipitation process.

EVALUATION OF REAGENTS FOR REMOVAL OF CALCIUM CHROMATE SPILLS

The GEND calcium chromate production area was designed to meet the NIOSH proposed standard[9] for Cr(VI) exposure of 1.0 g/m^3. Therefore, it is imperative that spills be cleaned as completely as possible since calcium chromate can become airborne on drying. The removal of these spills can be a problem due to the insolubility[6] of calcium chromate and the possibility of corrosion of the stainless steel equipment with the cleaning reagent.[10]

The solubility of calcium chromate in several reagents was investigated in an attempt to find a suitable clean-up reagent.[11] To compare the solubility, 100 ml of the desired reagent was added to 10-gram samples of calcium chromate, agitated for 15 min. at room temperature, and filtered. The filter paper containing the insoluble material was then dried at 135°C and reweighed to calculate the percent of insoluble material. All samples were taken from calcium chromate batches having similar chemical analyses. These analyses are shown in Table 10.

Table 10. Reagent Solubility Analysis

		$CaCrO_4$ CHEMICAL ANALYSES				% METALLIC IMPURITIES			
BATCH No.	%$CaCrO_4$	%Ca	%CO_2	%OH^-	pH	Si	Mg	Al	Fe
Blend 11	97.8	25.6	0.11	0.10	10.0	0.1	0.15	0.03	0.03
Blend 13	97.7	25.8	0.02	0.12	10.2	0.3	0.17	0.04	0.03

Results of hydrochloric, acetic and nitric acids are given in Table 11. Commercially available acids were used in each case and diluted to the indicated volume:volume ratio.

Table 11. $CaCrO_4$ Solubility in Acetic, Hydrochloric, and Nitric Acids

CONCENTRATION VOLUME: VOLUME	% ACID INSOLUBLE MATERIAL									
ACID	1:1	1:2	1:3	1:4	1:5	1:6	1:7	1:8	1:9	1:10
Acetic	0.48	0.49	0.46	0.54	0.52	0.49	0.56	0.68	0.77	1.27
Hydrochloric	-	0.11	0.21	0.39	0.37	0.32	0.31	0.22	0.24	0.25
Nitric	-	-	-	-	0.92	0.51	0.60	0.72	0.79	0.89

Table 12 shows results obtained with some organic acids. Duplicate samples were investigated for each concentration and the average percent of insoluble material reported, along with some observations on the reaction.

Salts of some organic acids, solutions of acetic acid and sodium acetate, and other possible complexing agents were also investigated. These results are reported in Table 13.

The dissolution of calcium chromate was most rapid in 1:1 hydrochloric acid with 1:1 acetic acid the next most rapid. The average percent of insoluble material for these two acids compared closely for concentrations of 1:3 to 1:7. The hydrochloric acid solutions were much more viscous than the acetic acid solutions and therefore more difficult to filter. The general trend for acetic acid is toward more insoluble material with less concentrated acid solutions. With hydrochloric acid concentrations of 1:4, 1:5, 1:6, and 1:7, more insoluble material remained than with either the higher or lower concentrations. However, the overall range of insoluble material for this acid was 0.11 to 0.39 percent. Concentrations of 1:1, 1:2, 1:3, and 1:4 nitric acid attacked the filter paper, making the experimental procedure impossible for these concentrations. The percent of insoluble material for a 1:5 nitric acid solution was high and the acid appeared to react with the filter paper to some extent. Other concentrations followed a trend toward more insoluble material for more dilute acids and compared closely with acetic acid data.

Table 12. $CaCrO_4$ Solubility in Some Organic Acids

REAGENT	CONCENTRATION	AVG. % INSOLUBLE MATERIAL	OBSERVATIONS
Tartaric Acid	2.0 M	-	Solution turned from brown color to blue-violet and boiled over due to effervescence. No insoluble material was observed but measurements could not be made.
Tartaric Acid	1.5 M	5.95	Solution turned blue-violet.
Tartaric Acid	1.0 M	34.11	Solution turned from mustard color to dark brown. Precipitate was green.
Tartaric Acid	0.5 M	53.48	Same color changes as above.
Citric Acid	4.0 M	0.49	Solution turns dark brown, effervesces and gradually turns blue-violet.
Citric Acid	3.5 M	2.15	Same color changes as above.
Citric Acid	3.0 M	1.74	Same color changes as above.
Citric Acid	2.5 M	0.88	Solution turned brown but not dark blue. Effervescence started ∿25 min. after acid was added to $CaCrO_4$.
Citric Acid	2.0 M	1.35	Same as above.
Citric Acid	1.5 M	1.75	Same as above.
Citric Acid	1.0 M	3.47	Same as above.
Citric Acid	0.5 M	3.75	No color change to dark brown.
Formic Acid	1:1 (Vol.:Vol.)	0.04	Solution turned from orange to brown.
Formic Acid	1:2 (Vol.:Vol.)	0.28	Same as above.
Formic Acid	1:3 " "	0.31	Same as above.
Formic Acid	1:4 " "	0.37	Solution turned orange-brown.
Formic Acid	1:5 " "	0.42	Solution clear orange.
Oxalic Acid	1.0 M	71.97	Solution turned dark brown.

The combination of 1-M sodium acetate and 1:1 acetic acid (Table 13) decreased the amount of insoluble material as compared with 1:1 acetic acid. However, with all other acetic acid concentrations, the addition of sodium acetate increased the percent of insoluble material.

Table 13. Other Reagents

REAGENT	CONCENTRATION	% INSOLUBLE MATERIAL
Sodium Formate	1 M	79.16
Sodium Citrate	1 M	63.79
Sodium Acetate	1 M	84.97
Sodium - EDTA	0.1 M	59.93
Sodium Oxalate	0.1 M	95.78
Sodium Thiosulfate	0.6 M	73.33
1:1 HAc/1 M NaAc*	1:1 (Volume:Volume)	0.09
1:2 HAc/1 M NaAc	1:1 " "	0.85
1:3 HAc/1 M NaAc	1:1 " "	2.01
1:4 HAc/1 M NaAc	1:1 " "	3.69
1:5 HAc/1 M NaAc	1:1 " "	4.76

*HAc - Acetic acid
NaAc - Sodium Acetate

The percent of insoluble material with several organic acids is reported in Table 12. The tartaric acid reaction with calcium chromate was most rapid, forming first a dark brown solution and then a dark blue-violet solution. Effervescence accompanied the brown to blue-violet change causing the solution to boil over the beaker. A solution of 1.5-M tartaric acid also yielded a blue-violet solution that was very viscous and contained some blue-green crystals. Color changes for the 1.0- and 0.5-M tartaric acid solutions did not include the blue-violet stage, remaining brown throughout the filtration with a green precipitate. These results are similar to those described by T. L. Rama Char for potassium dichromate and tartaric acid.[12]

Solutions of citric acid showed somewhat the same color changes. The more concentrated solutions, 4.0, 3.5, and 3.0 M turning brown and then blue-violet; the 2.0-, 1.5-, and 1.0-M concentrations remaining brown; and the 0.5-M solution remaining orange. The percentage of insoluble material for this acid followed a general trend toward more insoluble material with less concentrated solutions.

Formic acid solutions prepared from 90 percent formic acid stock solution were good dissolution agents for calcium chromate leaving very low amounts of insoluble material. The solution for the 1:1 concentration (45 percent formic acid) turned dark brown, while lower concentrations (1:4 and 1:5) remained orange.

Only 1-M oxalic acid was investigated since the percent of insoluble material was so high. Table 13 shows results obtained with some salts of organic acids. The percent of insoluble material was much higher in every case than the corresponding acid. Solutions of sodium-ethylenediaminetetraacetic acid and sodium thiosulfate were also investigated but did not appear to be promising reagents.

The blue-violet color change observed for the reaction of calcium chromate with tartaric and citric acids compares with work done by Oono[13] with chromium sulfate and sodium salts of citrate and tartrate. In this work, he observed the formation of complexes with adsorptions at 425 and 570 w/m, the latter absorption being associated with blue-violet solutions.

Several of the reagents investigated would be suitable for clean-up of calcium chromate spills on the basis of material dissolution. For dilute concentrations, hydrochloric acid is the most efficient; however, halide salts and halide acids destroy passivity of stainless steel with pitting and stress corrosion being encountered with concentrations less than 1 percent. The condensed vapors of dilute hydrochloric acid environments are usually more corrosive than the liquid phase.[14,10]

Austenitic stainless steels are fully resistant to attack by all concentrations of acetic acid at ambient temperatures. All concentrations of nitric acid tend to favor passivity of stainless steel at low temperatures, although the vapors can be slightly corrosive in high concentrations. All organic acids used in the study are noncorrosive with stainless steel.[10]

Because of the very slight difference in the efficiency of the dissolution process with acetic, hydrochloric and nitric acids, and the corrosion caused by even small amounts of hydrochloric acid, it was recommended that either dilute acetic or nitric acid solutions be used in cleaning spills in the GEND calcium chromate production area.

EVALUATION OF METHOD FOR DETERMINING HYDROXIDE IN $CaCrO_4$ SAMPLES

One of the impurities seen in highest concentration in calcium chromate is the hydroxide ion. The GEND process[2] for calcium chromate involves the use of slaked calcium oxide as the precipitating agent, which is the most likely source of the hydroxide impurity. The specification for thermal battery grade calcium chromate limits the hydroxide ion concentration, reported as calcium hydroxide, to a maximum of 1 percent.

The method routinely used for hydroxide determination at GEND[15] involves the direct titration of the hydroxide ion with dilute sulfuric acid to an end point of pH 9.1. Characterization of some of the GEND produced calcium chromate revealed an excess of calcium of about 0.5 percent. This excess was above the total calcium found in calcium chromate, calcium hydroxide and calcium carbonate. Thermal analysis data also showed evidence that indicated the excess calcium could be due to undetected calcium hydroxide. For these reasons, a back-titration method of determining hydroxide ion was investigated and at the same time the direct titration method was reevaluated.[16]

The back-titration method for determining hydroxide ion involves the addition of excess perchloric acid and titration of the excess acid with sodium hydroxide. This method is described in detail in the above referenced report.

Samples obtained from six vendors were analyzed for hydroxide ion by the back-titration method. These results are shown in Table 14. This table also includes hydroxide ion concentrations obtained by the direct titration method and carbon dioxide concentrations determined by a gas evolution method.[17] These data show that for Vendors 2, 4, and 5, both titration methods gave similar results. Results for other vendors indicate that the carbon dioxide content perhaps affected the back-titration method results. The percent of hydroxide ion for GEND calcium chromate determined by the back-titration method was very similar, in many cases, to the total of the percent of carbon dioxide and percent of hydroxide ion determined by the direct titration method.

Table 14. Comparison of Hydroxide Content Found By Direct and Back-Titration Methods in Calcium Chromate

Description or Sample Number	Percent Hydroxide		Carbon Dioxide (%)
	Back-Titration	Direct	
Vendor 1	0.36	0.18	0.1
Vendor 2	4.1	4.2	0.7
Vendor 3	2.55	-	2.5
Vendor 4	0.08	0.11	0.04
Vendor 5	N.D.*	N.D.*	N.D.*
Vendor 6	2.04	0.72	1.3
GEND 146	0.42	0.07	0.33
GEND 170	0.45	0.12	0.32
GEND 136	0.40	0.10	0.20
GEND 140	0.45	0.07	0.26
GEND 141	0.43	0.07	0.31
GEND 121	0.34	0.08	0.07
GEND 159	0.56	0.20	0.73
GEND 162	0.46	0.22	0.33
GEND 134	0.32	0.07	0.13
GEND 148	0.39	0.16	0.26
GEND 113	0.14	0.08	0.02
GEND 112	0.12	0.05	0.01
GEND Blend 243	0.58	0.19	0.64
GEND Blend 244	0.74	0.19	0.70
GEND Blend 245	0.49	0.18	0.41
GEND Blend 246	0.44	0.15	0.36
GEND Blend 247	0.58	0.16	0.25
GEND Blend 248	0.44	0.18	0.23

*None Detected

Since the addition of an acid to the calcium chromate sample can result in the conversion of the carbonate to bicarbonate, carbonic acid, and/or carbon dioxide, the effect of varying the amount of acid added as excess on the results of the back-titration method was investigated. Results are given in Table 15. The percent of hydroxide ion as determined by this method increased as the volume of acid added increased. Sample GEND 245 contained 0.41 percent carbon dioxide and GEND Blend 3 contained 0.01 percent carbon dioxide. GEND Blend 3 showed only a small variation in the percent of hydroxide ion with increases in acid concentration. From these data it was concluded that carbonate concentration has an effect on the percent of hydroxide ion determined from the back-titration method.

Table 15. The Effects of Total Acid Used in the Back-Titration Method for Hydroxide

Sample Number	Volume of Acid Added (ml)	Solution (pH)	Hydroxide Content (%)
GEND 245	1.0	8.6	0.30
	2.0	7.7	0.36
	3.0	7.5	0.37
	4.0	7.4	0.40
	5.0	7.3	0.42
	10.0	6.9	0.49
GEND Blend 3	10.0	6.8	0.25
	20.0	6.2	0.18
	30.0	5.7	0.22
	40.0	2.8	0.32

The effect of varying the calcium chromate sample size on the percent of hydroxide ion obtained by the back-titration method was also evaluated. Results are shown in Table 16.

As sample size increased, the hydroxide ion concentration decreased, probably due to an increase in insoluble material.

Table 16 also shows results obtained for percent recoveries of hydroxide ion when the sample and procedure variables are held constant.

Results from the preceding data indicated that the back-titration method would not be reliable for routine application where the carbonate ion concentration was either not known or varied over an unknown range. For the sample GEND Blend 3, where the percent of carbon dioxide

Table 16. The Effects of Sample Size and Calcium Hydroxide Concentration on the Back-Titration of Hydroxide in Calcium Chromate GEND Blend 3

Sample Weight (g)	Acid Volume Added (ml)	Initial Sample (pH)	Spike $Ca(OH)_2$			Total Hydroxide (%)
			Added (mg)	Recovery (mg)	Recovery (%)	
I. Varying Sample Size						
0.2520	10.0	5.8	None	-	-	0.43
0.2726	10.0	6.5	None	-	-	0.43
0.4769	10.0	6.3	None	-	-	0.29
0.5467	10.0	6.8	None	-	-	0.25
0.7652	10.0	6.4	None	-	-	0.21
0.7959	10.0	6.8	None	-	-	0.22
1.0245	10.0	6.5	None	-	-	0.20
II. Recovery of Added $Ca(OH)_2$						
0.5060	10.0	6.4	2.18	2.13	98	0.46
0.5348	10.0	6.5	4.36	4.46	102	0.65
0.5713	10.0	6.6	6.54	6.29	96	0.78
0.5178	10.0	6.4	8.72	8.16	94	0.99

(0.01 percent) was very low, the method was reliable. For these reasons the direct titration method was reevaluated using GEND 245 calcium chromate. The results are shown in Table 17. This sample contained 0.41 percent carbon dioxide. An average calcium hydroxide recovery of 93 percent was obtained for two samples spiked with $Ca(OH)_2$, and an average recovery of 87 percent was obtained for two samples spiked with CaO. No effects were detected from added calcium carbonate using this method.

From these results it was concluded that the direct titration method was better for routine application where the relation of sample size and carbonate ion concentration to quantity of acid used could not be easily controlled.

Table 17. Recovery of Calcium Hydroxide and Calcium Oxide by Direct Titration Method in Sample Number 245

Sample Weight (g)	Calcium Hydroxide* Added (mg)	Calcium Hydroxide* Found (mg)	Calcium Hydroxide* Recovery (%)	Calcium Oxide** Added (mg)	Calcium Oxide** Found (mg)	Calcium Oxide** Recovery (%)
0.4980	39.5	34.9	88	-	-	-
0.5037	10.2	10.0	98	-	-	-
0.5051	-	-	-	12.9	11.4	88
0.5050	-	-	-	14.2	12.2	86
Average Recovery			93			87

*Baker "Analyzed" reagent chemical

**Fisher "Certified" reagent chemical

CONCLUSIONS

This work led to following conclusions.

(1) The optimum drying time and temperature for GEND calcium chromate in addition to process drying should be 600°C for 4 hours. The product should be dried according to this process before analysis. Gases evolved during this drying period include carbon dioxide and water vapor.

(2) The purity of the lime used directly affects the purity of the calcium chromate produced. For this study the product having highest purity was obtained with technical grade lime.

(3) The preparation of calcium chromate by the addition of ammonium chromate to slaked lime results in a product of lower purity than that produced with the standard procedure. The impurity with the highest concentration was hydroxide ion. This concentration could probably be reduced by a longer digestion time or higher digestion temperature.

(4) Recommened reagents for clean-up of calcium chromate spills in the process area include either dilute acetic or nitric acids. Hydrochloric acid should not be used due to its corrosiveness with stainless steel.

(5) The method of determining hydroxide ion concentration by direct titration was found to be more reliable than an indirect titration method which was dependent on the relation of carbonate ion concentration, sample size and amount of acid added for back titration.

ACKNOWLEDGMENTS

The author wishes to acknowledge the work of R. Antepenko in evaluating hydroxide ion analysis methods, G. K. Chivington for analysis of calcium chromate samples used in this study, and T. Mehrhoff for thermal desorption work.

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APPENDIX A

RATES OF EVOLUTION

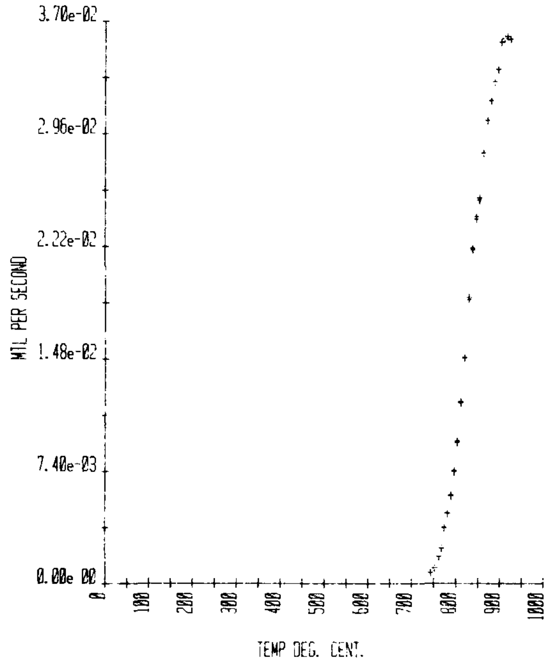

Figure A-1. Rate of Evolution - Mass 32 - $CaCrO_4$ Production Facility 26-1. Not vacuum dried.

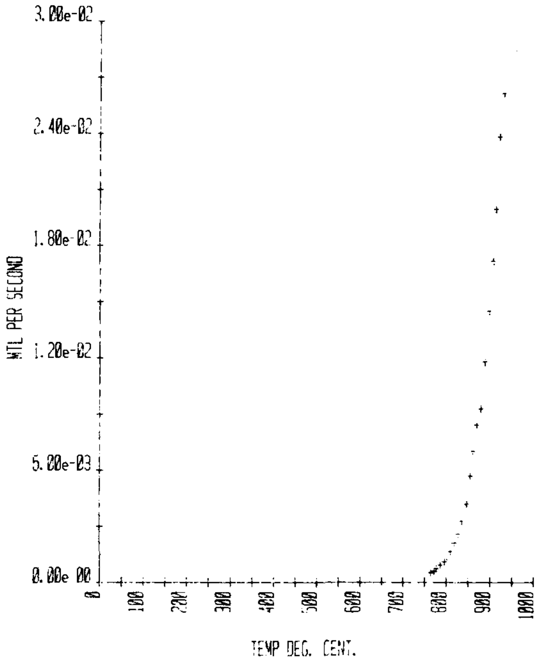

Figure A-2. Rate of Evolution - Mass 32 - $CaCrO_4$ Production Facility 27-1. Not vacuum dried.

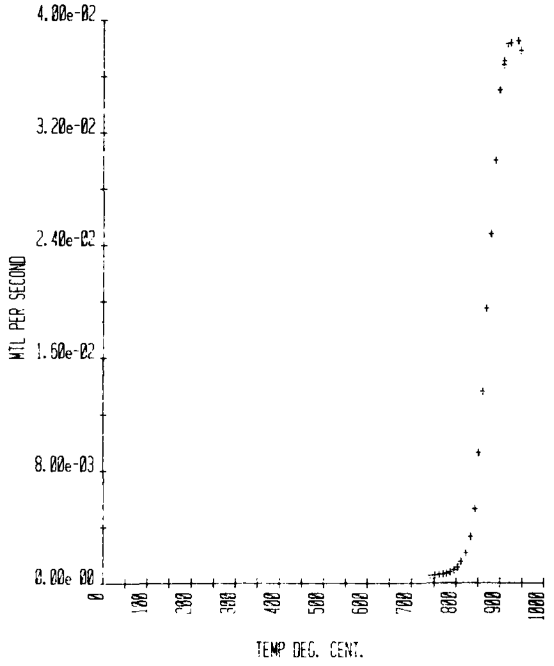

Figure A-3. Rate of Evolution - Mass 32 - $CaCrO_4$ Blend 12

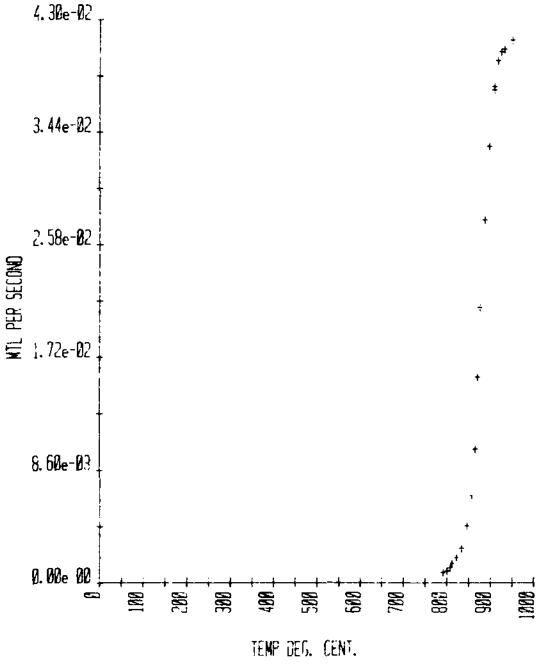

Figure A-4. Rate of Evolution - Mass 32 - $CaCrO_4$ 243

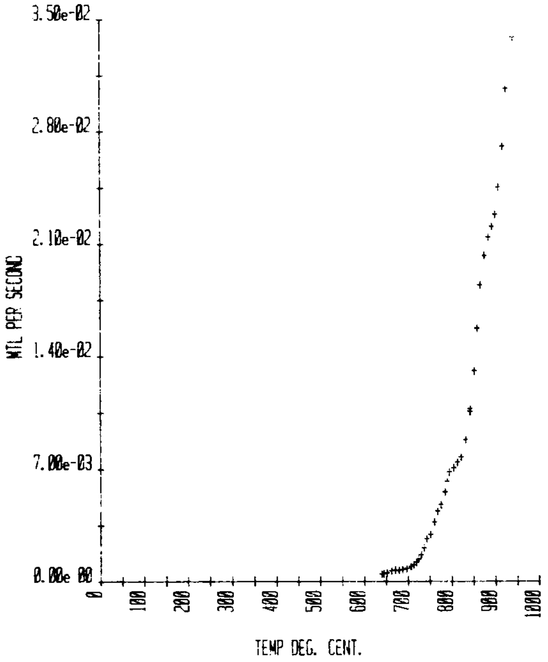

Figure A-5. Rate of Evolution - Mass 32 - $CaCrO_4$ Var-Lac-Oid No. 2

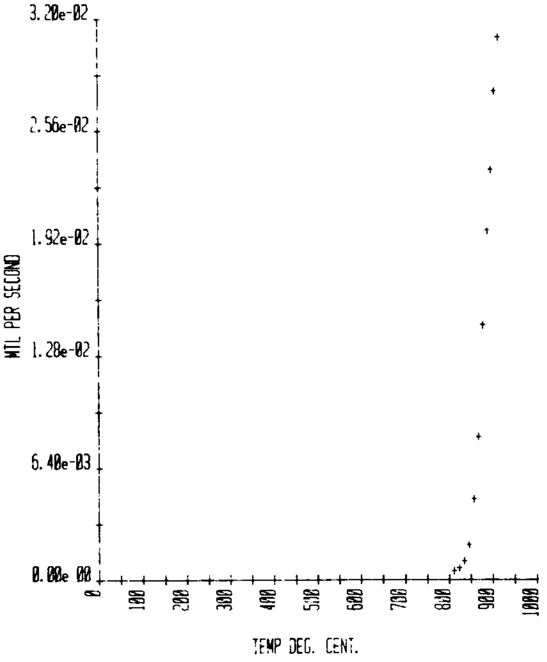

Figure A-6. Rate of Evolution - Mass 32 - $CaCrO_4$ Production Facility 929. Not vacuum dried.

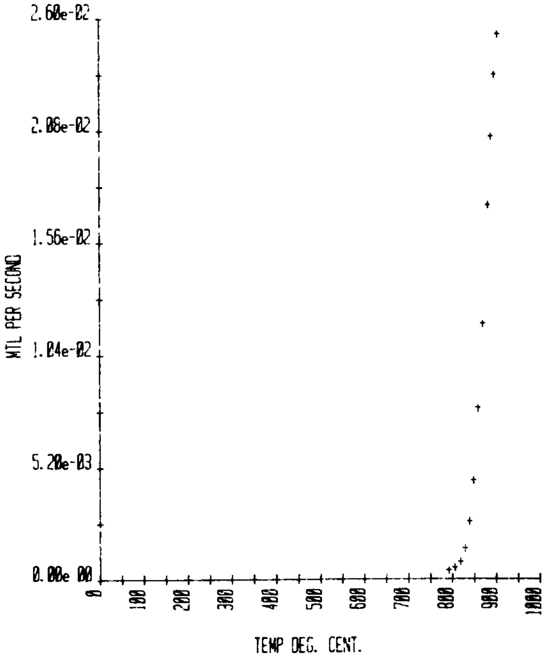

Figure A-7. Rate of Evolution - Mass 32 - $CaCrO_4$ Production Facility 943. Vacuum dried.

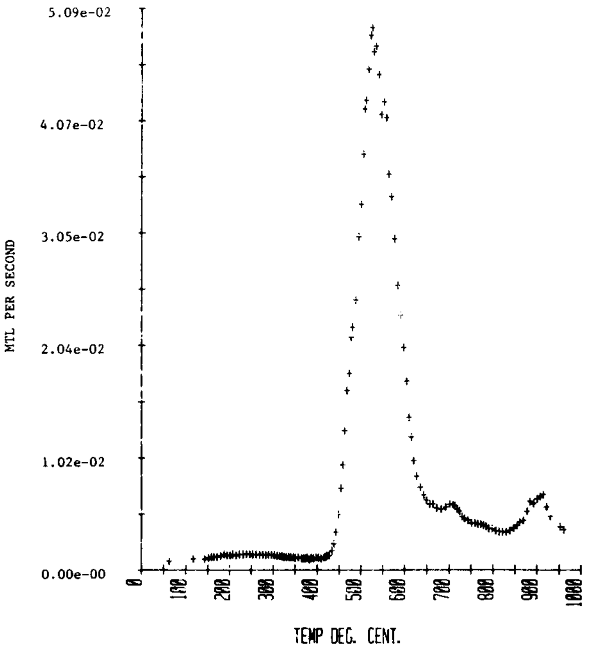

Figure A-8. Rate of Evolution - Mass 18 - $Ca(OH)_2$

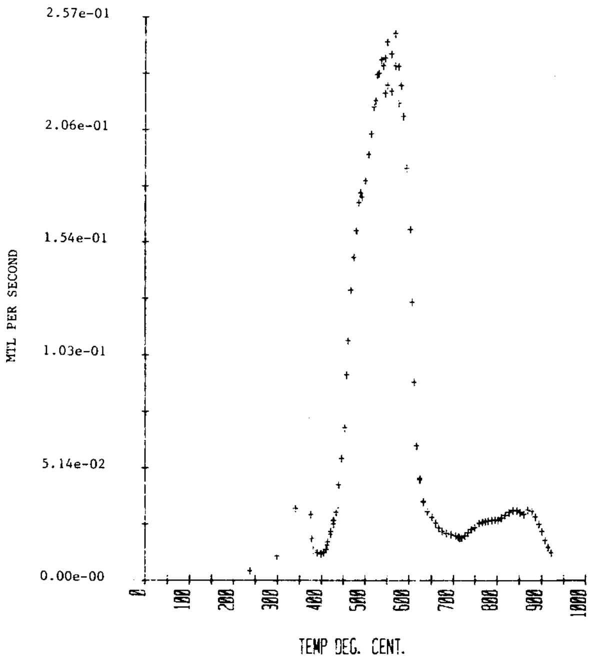

Figure A-9. Rate of Evolution - Mass 18 - $CaCrO_4$ Production Facility 26-1. Not vacuum dried.

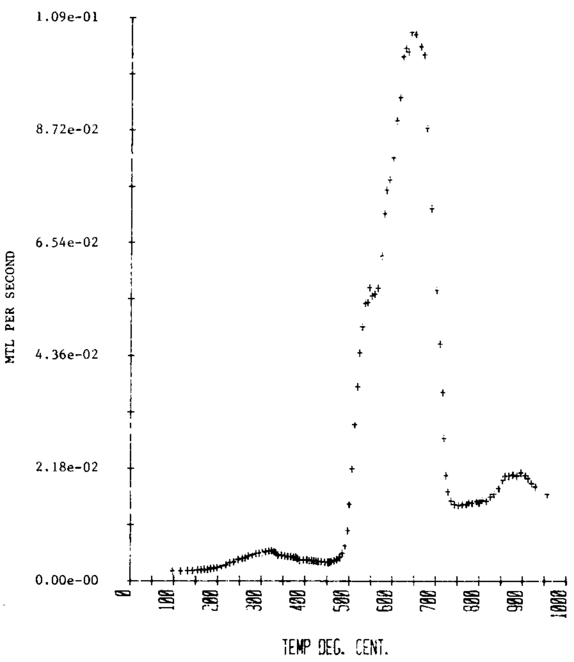

Figure A-10. Rate of Evolution - Mass 18 - $CaCrO_4$ Production Facility 27-1. Not vacuum dried.

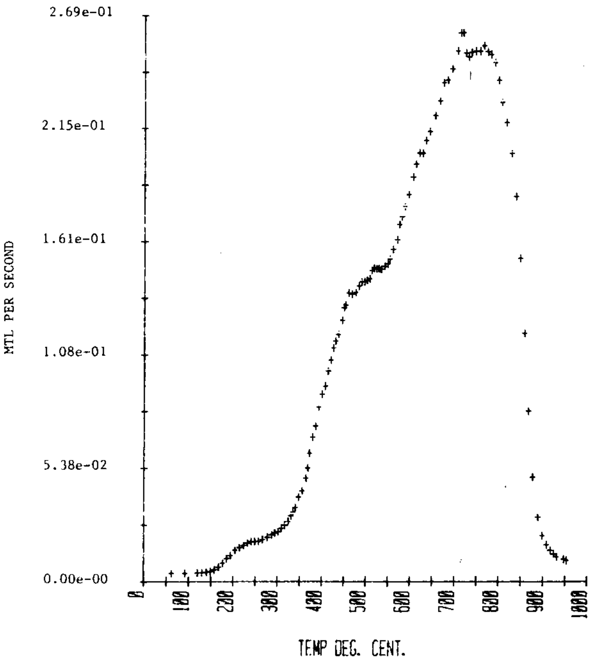

Figure A-11. Rate of Evolution - Mass 18 - $CaCrO_4$ Blend 12

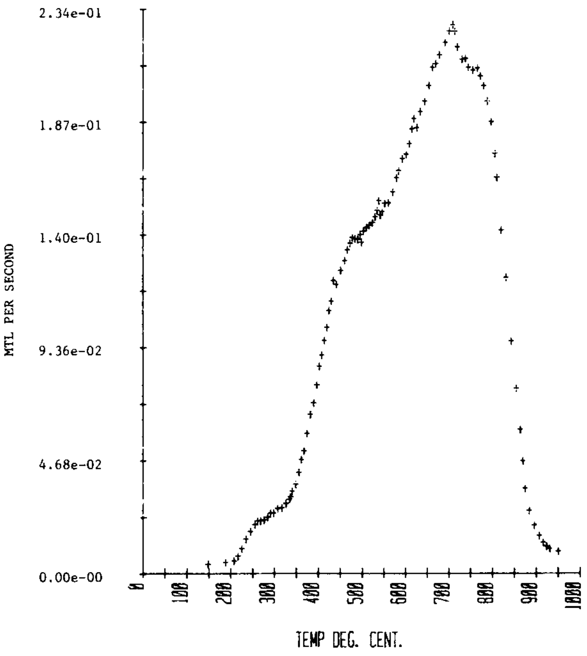

Figure A-12. Rate of Evolution Mass 18 - $CaCrO_4$ 243

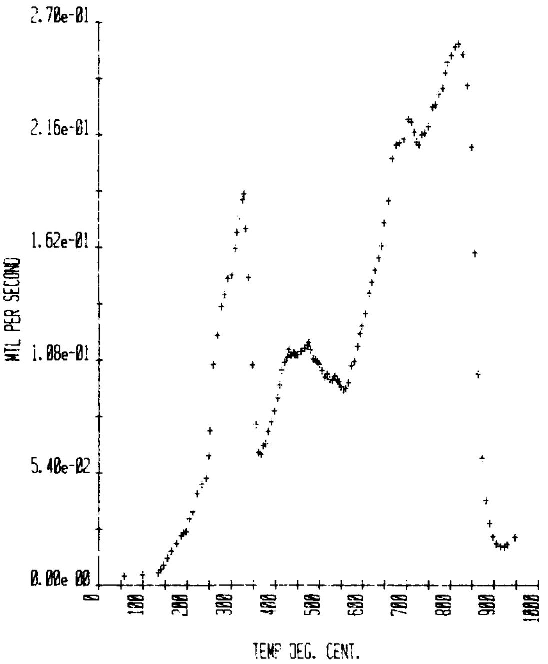

Figure A-13. Rate of Evolution - Mass 18 - $CaCrO_4$ Var-Lac-Oid 2

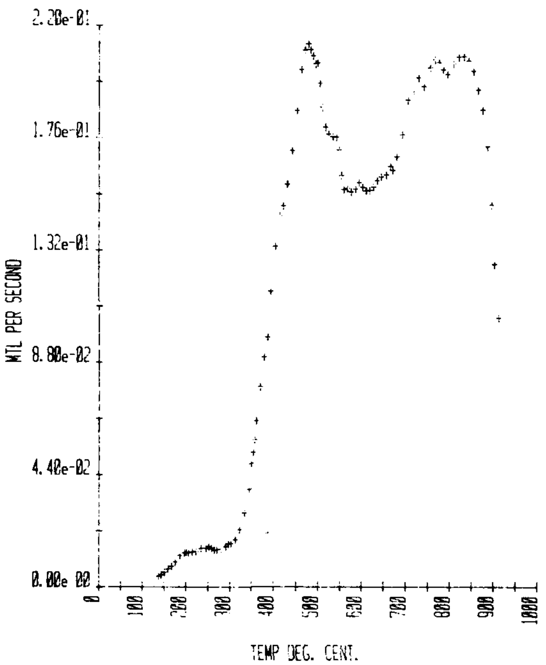

Figure A-14. Rate of Evolution - Mass 18 - $CaCrO_4$ Production Facility 929. Not vacuum dried.

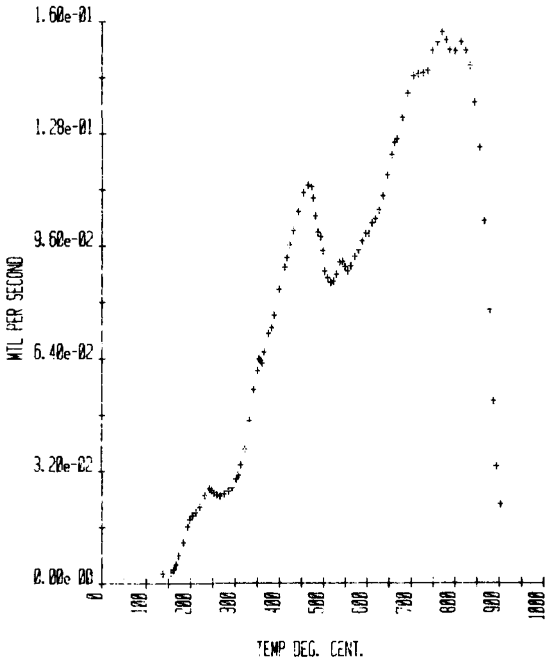

Figure A-15. Rate of Evolution - Mass 18 - $CaCrO_4$ Production Facility 943. Vacuum dried.

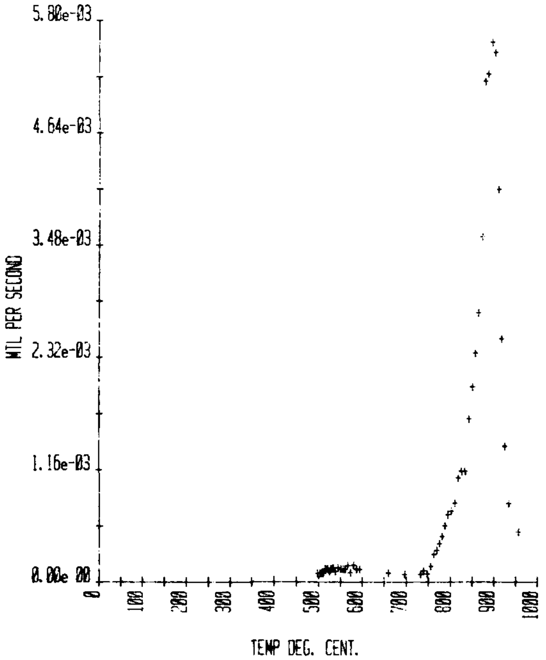

Figure A-16. Rate of Evolution - Mass 44 - $CaCO_3$

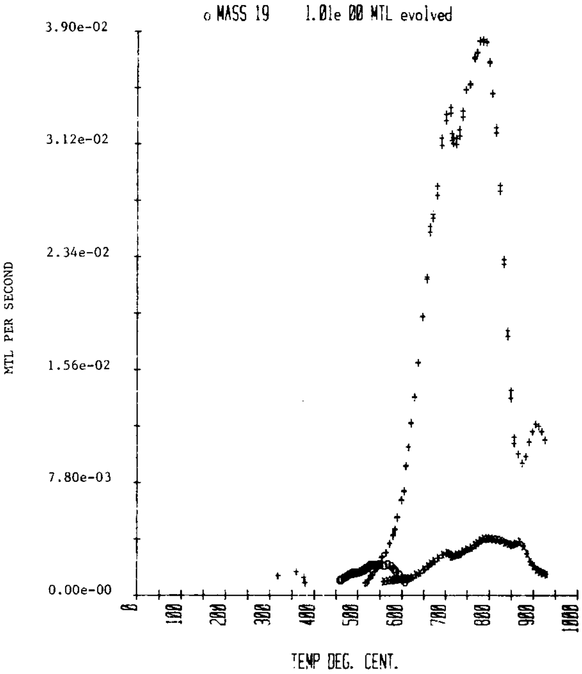

Figure A-17. Rate of Evolution - Mass 44 - $CaCrO_4$ Production Facility 26-1. Not vacuum dried.

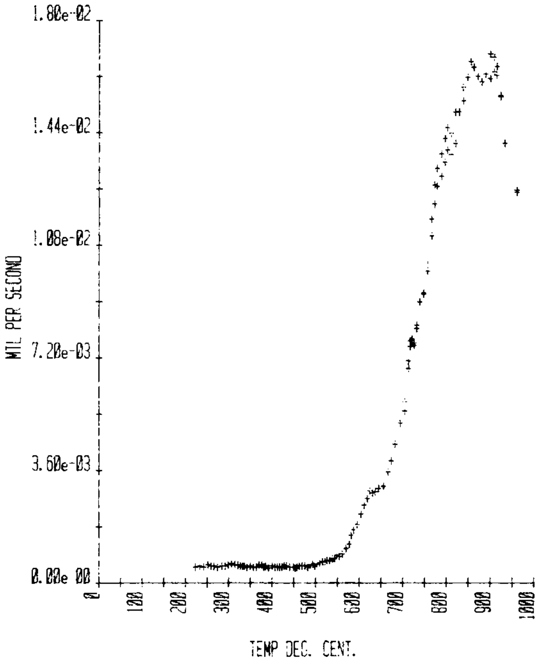

Figure A-18. Rate of Evolution - Mass 44 - $CaCrO_4$ Production Facility 27-1. Not vacuum dried

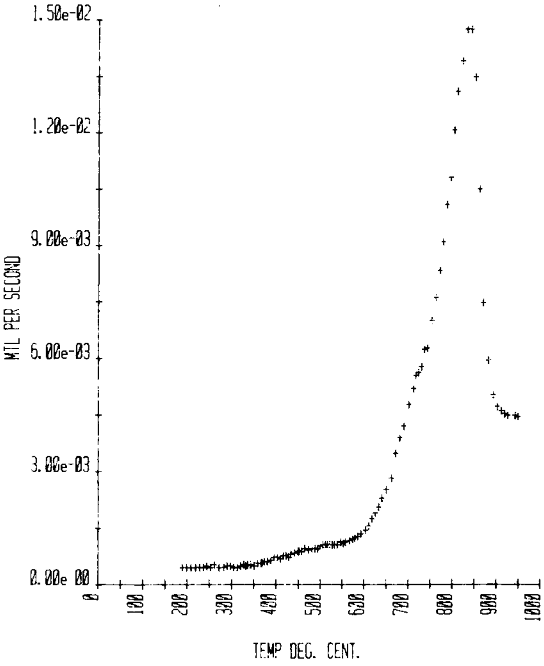

Figure A-19. Rate of Evolution - Mass 44 - $CaCrO_4$ Blend 12

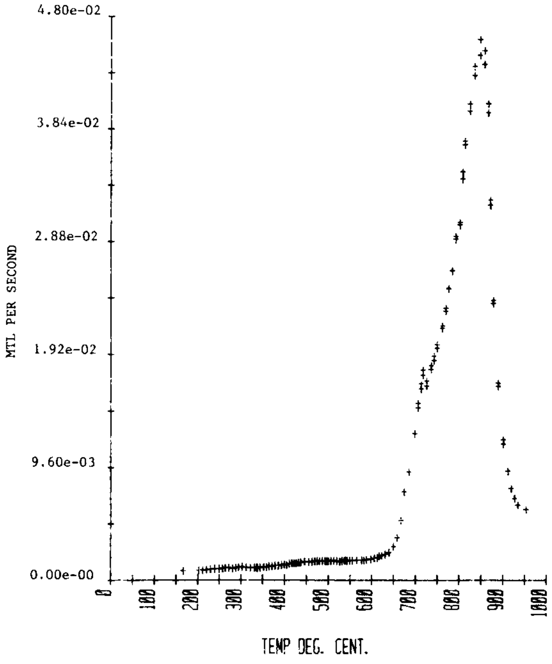

Figure A-20. Rate of Evolution Mass 44 - $CaCrO_4$ 243

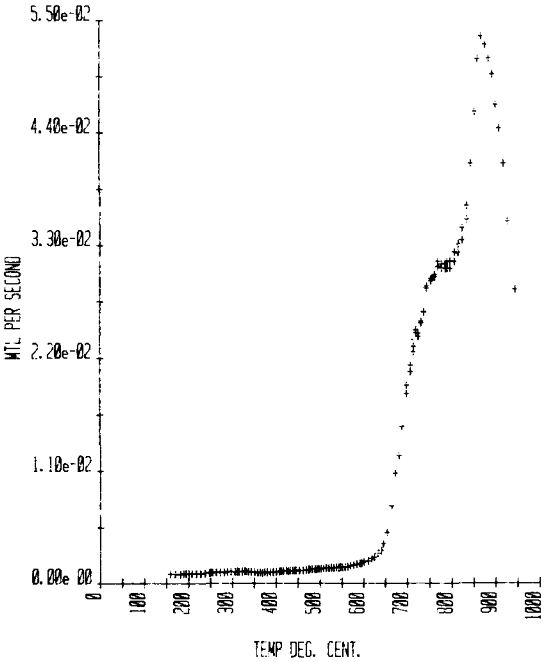

Figure A-21. Rate of Evolution - Mass 44 - $CaCrO_4$ Var-Lac-Oid 2

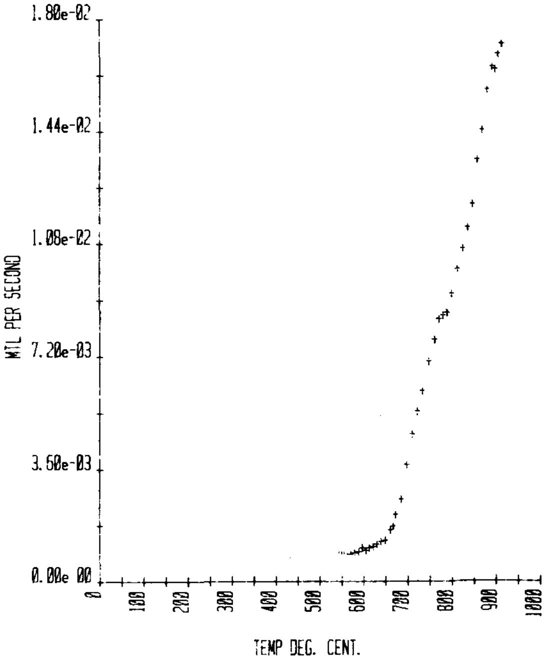

Figure A-22. Rate of Evolution - Mass 44 - $CaCrO_4$ Production Facility 929. Not vacuum dried

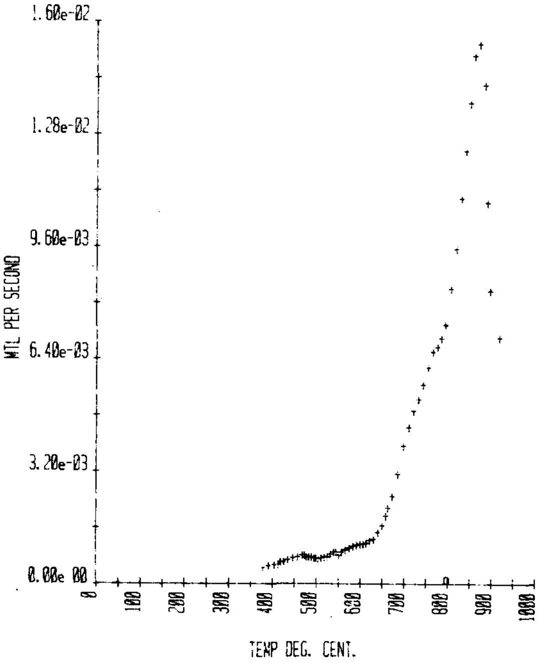

Figure A-23. Rate of Evolution - Mass 44 - $CaCrO_4$ Production Facility 943. Vacuum dried.

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