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Identification of Calcium Chromate Samples

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Prepared by Sandia Laboratories, Albuquerque New Mexico 87115
and Livermore, California 94550 for the United States Energy Research
and Development Administration under Contract AT (29-1)-789

Printed July 1977

Sandia Laboratories

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IDENTIFICATION OF CALCIUM CHROMATE SAMPLES

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ABSTRACT

Anhydrous calcium chromate (CaCrO_4), produced by Allied Chemical Corporation, has been employed as the active cathode material in Sandia thermal batteries for many years. After being informed by Allied that they would no longer manufacture CaCrO_4 , Sandia placed a contract with General Electric Neutron Devices Department (GEND) to develop a procedure for the synthesis of anhydrous calcium chromate. During this development, a study of washing procedures used indicated that the GEND-made calcium chromate was not anhydrous. Even though chemical analyses of the GEND material after heating at 400°C indicated it was similar to the Allied CaCrO_4 , the solubility of GEND calcium chromate in water before heating was 4 to 5 times that of Allied CaCrO_4 . Emission spectroscopy of GEND calcium chromate showed no unusual results. Thermogravimetry and mass spectroscopy experiments showed a water loss of nearly 8% between 150 and 200°C for the GEND material. X-ray diffractometry gave a pattern very different from that for anhydrous CaCrO_4 but similar to a calculated pattern for $\text{CaCrO}_4 \cdot \text{H}_2\text{O}$. These results plus important literature information resulted in the conclusion that the material produced by the GEND procedure is primarily $\text{CaCrO}_4 \cdot \text{H}_2\text{O}$ with a small amount (<25%) of CaCrO_4 present. Heating the material to 200°C results in the rapid formation of anhydrous CaCrO_4 .

ACKNOWLEDGMENT

The author wishes to acknowledge the analytical efforts of W. W. Welbon and B. M. Dillard of GEND; the emission spectroscopy work of J. F. Wolcott, the mass spectrometry studies of F. J. Conrad, the solubility measurements of F. W. Reinhardt, and the X-ray diffraction experiments by G. T. Gay, all of Sandia Laboratories.

IDENTIFICATION OF CALCIUM CHROMATE SAMPLES

Introduction

Nearly all thermal batteries which have been, and are being, developed at Sandia Laboratories employ the electrochemical system $\text{Ca/LiCl-KCl-CaCrO}_4/\text{Fe}^1$. Anhydrous calcium chromate (CaCrO_4) serves as the active cathode material in the system with the Cr(VI) being reduced at the cathode. For many years this fundamental ingredient in Sandia thermal batteries had been supplied by Allied Chemical Corporation, Morristown, NJ. However, in 1974 Sandia was informed by Allied that they would no longer manufacture and market CaCrO_4 . Sandia immediately began a search for other suppliers of CaCrO_4 and simultaneously placed a contract with General Electric Company, Neutron Devices Department, St. Petersburg, FL, (GEND) for the development of a procedure for the synthesis of anhydrous calcium chromate.

Under Sandia P. O.'s 64-3144 and 02-9193, GEND developed a procedure for producing CaCrO_4 according to the following reaction scheme:

The precipitated calcium chromate was washed, collected by filtration, and dried for 24 hours at 110°C . The product, after being heated 4 hours at 400°C , was analyzed for Cr(VI), Ca, OH^- , $\text{CO}_3^{=}$, metallic impurities, surface area, and particle size distribution. Based on the results of these analyses, the calcium chromate synthesized by GEND appeared equivalent to the anhydrous CaCrO_4 sold by Allied Chemical.

Because some questions arose concerning the procedures used to wash the GEND CaCrO_4 , these washing techniques were investigated at Sandia. During these investigations, it was observed that the solubility of air dried GEND calcium chromate in water was much greater than the previously determined solubility of anhydrous CaCrO_4 . Because of this anomaly, an investigation of the GEND calcium chromate was undertaken to determine the cause of this solubility difference. This determination involved solubility measurements, emission spectroscopy, thermogravimetric analysis, mass spectrometry, X-ray diffractometry, and a survey of CaCrO_4 literature.

Results

Chemical Analyses by GEND

The results of the chemical analyses performed by GEND on the calcium chromate sample after baking it 4 hours at 400°C are given in Table I. These results are very similar to those obtained for Allied CaCrO_4 .

TABLE I

Results of GEND Chemical Analyses for Calcium Chromate
Baked at 400°C for 4 Hours

% Cr (VI)	32.6
% CaCrO_4 [based on Cr(VI)]	97.7
% Ca	26.0
% OH^-	0.05
% Ca(OH)_2 [based on OH^-]	0.2
% $\text{CO}_3^{=}$	0.5
% CaCO_3 [based on $\text{CO}_3^{=}$]	0.8

Solubility

A ~10 g sample of the unheated or raw GEND calcium chromate totally dissolved (except for ~1% CaCO_3 impurity) in 240 ml of deionized water after 30 seconds stirring followed by an 18-hour set time at 25°C. Based on literature data⁽²⁾ and unpublished data generated in our laboratory, one would expect only ~2 g of anhydrous CaCrO_4 to dissolve in that volume of water under those conditions. If the calcium chromate-water mixture were agitated until the equilibrium solubility were attained, still only 4.9 g of anhydrous CaCrO_4 would dissolve in 240 ml water at 25°C. The time required to reach this equilibrium condition would be in excess of 200 hours.

Emission Spectroscopy

A semi-quantitative determination of the metallic impurities in the GEND CaCrO_4 was made using emission spectroscopy. The results are given in Table II. These results are very similar to those observed for Allied calcium chromate and do not suggest any anomaly with the GEND material.

TABLE II
Results of Emission Spectroscopy Analysis for
GEND Calcium Chromate

<u>Element</u>	<u>Concentration (ppm)</u>
Al	200
Fe	150
K	40
Li	4
Mg	1000
Mn	20
Na	20
Si	1000
Sr	80
Ti	25

Thermogravimetric Analysis

Calcium chromate samples as received from both GEND and Allied Chemical were analyzed using thermogravimetry (TG). The GEND CaCrO_4 had not been previously heated; it is not known if the Allied CaCrO_4 was heated prior to shipment. These samples were heated from room temperature to $\sim 900^\circ\text{C}$ in a room air atmosphere at a constant heating rate of $6.1^\circ\text{C}/\text{min}$. The resulting TG curves are shown in Figure 1. The GEND calcium chromate exhibited a very large weight loss between 150 and 195°C ($\sim 7.5\%$ loss) and a total loss of 10.5% to 900°C . By contrast, the Allied material lost $\sim 0.1\%$ up to 195°C and a total of $\sim 1.7\%$ to 900°C . The temperature of the large (7.5%) weight loss in the GEND calcium chromate suggested the possibility of water of crystallization.

Mass Spectrometry

Although the temperature ($150\text{--}195^\circ\text{C}$) of the weight loss observed in the TG studies is typical of that for the loss of water of hydration (or crystallization), it was necessary to positively identify the gaseous product(s) responsible for this weight loss. For this purpose, the gas liberated between 150 and 195°C was analyzed using mass spectrometry. The results confirmed the fact that this was indeed water vapor.

Figure 1. TG Curves for GEND and Allied Calcium Chromate Samples

X-ray Diffractometry

The X-ray diffraction pattern obtained for unheated GEND calcium chromate was very complex. Analysis of the pattern indicated the presence of a small amount of anhydrous CaCrO_4 . However, the major phase present could not be identified. Compounds specifically sought, but not found, were the various starting materials and possible intermediate and side products, including CrO_3 , CaO , Ca(OH)_2 , $(\text{NH}_4)_2\text{CrO}_4$, $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$, CaCr_2O_7 , and $\text{CaCrO}_4 \cdot 2\text{H}_2\text{O}$. $\text{CaCrO}_4 \cdot 2\text{H}_2\text{O}$ is the only hydrated form of calcium chromate for which there exists an X-ray pattern in the literature.

As received calcium chromate samples from BDH (British Drug House) and Allied, as well as a sample prepared in our laboratory from CaCO_3 and $\text{Na}_2\text{CrO}_4^{(3)}$, were also examined using X-ray diffractometry. The patterns for all three samples were identical to the literature pattern for anhydrous CaCrO_4 .

Two additional samples of the GEND calcium chromate, one heated to 200°C during the TG investigation and the other heated for 4 hours at 400°C, were analyzed by X-ray diffraction. In both of these cases the patterns were also in total agreement with that for anhydrous CaCrO_4 . From the X-ray results, it was apparent that the GEND material was something other than anhydrous CaCrO_4 prior to heating, and that after heating to 200°C, the material had been converted to CaCrO_4 .

Literature Review of Hydrated Calcium Chromate

The results of the TG, mass spectrometry, and X-ray diffractometry studies suggested that the GEND calcium chromate might be a hydrated species. Little has been published concerning the hydrates of calcium chromate, but the work of Mylius and von Wrochem⁽²⁾ contains a significant amount of information which is pertinent to this investigation. A brief summary of some of that information follows.

Four hydrates of CaCrO_4 are known to exist. Their composition and crystalline form are shown in Table III.

TABLE III
Composition and Crystalline Form of
Calcium Chromate Hydrates

<u>Compound</u>	<u>Formula</u>	<u>Crystalline Form</u>
α · dihydrate	$\text{CaCrO}_4 \cdot 2\text{H}_2\text{O}$	monoclinic
β · dihydrate	$\text{CaCrO}_4 \cdot 2\text{H}_2\text{O}$	orthorhombic
monohydrate	$\text{CaCrO}_4 \cdot \text{H}_2\text{O}$	orthorhombic
hemihydrate	$\text{CaCrO}_4 \cdot 1/2\text{H}_2\text{O}$	octahedral

The α · dihydrate is the least stable, the β · hydrate is the second least stable, the monohydrate is next, and the hemidhydrate is the most stable. All four of these compounds will ultimately decompose to form the anhydrous CaCrO_4 .

The particular compound which is produced during the synthesis of calcium chromate depends on the reactants used, the concentration of the reactants, the temperature of the reaction mixture, and the digestion time.

All four hydrates are more soluble in H_2O than is anhydrous CaCrO_4 . The monohydrate is approximately 4 to 5 times as soluble as the anhydrous. The monohydrate contains 10.3% H_2O .

X-ray patterns are available for only the β · dihydrate.

The crystal structure of $\text{CaCrO}_4 \cdot \text{H}_2\text{O}$ is known to be orthorhombic,⁽²⁾ and the lattice parameters for the monohydrate are known to be: $a = 8.11$, $b = 12.77$, and $c = 7.99$ ⁽⁴⁾. From these data, d-spacings were calculated using a computer program developed at Sandia⁽⁵⁾ and based on plane spacings equations as defined by Cullity⁽⁶⁾. This technique gives all the d-spacings but yields no information concerning relative intensities. The results of these calculations are shown in Table IV, along with the observed d-spacings for the raw GEND calcium chromate sample and the strongest two lines for anhydrous CaCrO_4 . It can be observed from Table IV that, with one exception, all the lines observed in the X-ray pattern for GEND calcium chromate correspond to d-spacings calculated for $\text{CaCrO}_4 \cdot \text{H}_2\text{O}$. That one exception is a very, very weak line at $2.68 \text{ \AA}$, and this corresponds to the second strongest line for anhydrous CaCrO_4 .

Summary and Conclusions

The solubility data, X-ray diffraction results, and thermogravimetric analyses all indicated that the raw GEND calcium chromate was a material other than CaCrO_4 . However, chemical analyses of GEND calcium chromate heated to 400°C gave results typical of known anhydrous calcium chromate samples previously analyzed. X-ray diffraction of GEND samples which had been heated to either 200 or 400°C indicated that conversion to CaCrO_4 had taken place. Thermogravimetric results showed a large weight loss for GEND calcium chromate between 150 and 195°C , and mass spectroscopy identified H_2O vapor as the cause of this weight loss. Emission spectroscopy showed no unusually high levels of metallic impurities in the raw GEND material. The literature review revealed the existence of four hydrated calcium chromate compounds and gave solubility data for each hydrate.

The TG and solubility results, in view of the literature data, point to $\text{CaCrO}_4 \cdot \text{H}_2\text{O}$ as the likely material produced by GEND. A calculated X-ray diffraction pattern for the monohydrate is in good agreement with the experimentally obtained pattern for GEND calcium chromate. There is some evidence in the X-ray pattern for the presence of a small amount of anhydrous CaCrO_4 in the sample. This is supported by the fact that less water of hydration is detected by TG (7.8% H_2O) than would be expected for $\text{CaCrO}_4 \cdot \text{H}_2\text{O}$ (10.3% H_2O).

The conclusion from these analyses is that the raw GEND material consists primarily of $\text{CaCrO}_4 \cdot \text{H}_2\text{O}$ with a lesser quantity of anhydrous CaCrO_4 (up to 25%) present. The monohydrate is converted to CaCrO_4 by heating to 200°C . These results are in total agreement with all of the analytical results, as well as with the available literature data.

TABLE IV

X-ray Diffraction d-spacings for GEND Calcium Chromate, $\text{CaCrO}_4 \cdot \text{H}_2\text{O}$ and CaCrO_4

Observed d-spacings for GEND Calcium Chromate		Calculated d-spacings for $\text{CaCrO}_4 \cdot \text{H}_2\text{O}$ (Å)	Literature d-spacings for two strongest lines in CaCrO_4 (Å)
d-spacing (Å)	Intensity (strongest = 10)		
6.4	2	6.39	
5.2	3	5.20	
		4.99	
4.20	3	4.25	
		4.06	
3.98	1	3.99	
3.82	1	3.86	
3.59	3	3.58	3.62 strongest
		3.48	
3.46	10	3.45	
		3.42	
		3.41	
		3.39	
3.18	3	3.19	
		3.15	
		3.12	
		2.97	
2.92	3	2.94	
		2.85	
		2.78	
		2.77	
		2.76	
2.74	6	2.74	
2.68	1		2.68 2nd strongest
2.59	1	2.60	
		2.51	
		2.50	
		2.49	
2.48	1	2.48	
2.44	3	2.46	
		2.39	
		2.38	
2.37	4	2.37	
		2.36	
		2.35	
		2.33	
2.23	1	2.24	
		2.21	
		2.19	
2.18	1	2.18	
		2.16	
		2.13	
		2.12	
		2.11	
		2.10	
		2.09	
2.08	1	2.08	
		2.06	
		2.05	
2.02	1	2.03	
		2.00	

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