

Montana Tech Library

**Digital Commons @ Montana Tech**

---

Bachelors Theses and Reports, 1928 - 1970

Student Scholarship

---

Spring 5-1956

## **Synthetic Manganese Dioxide Production**

Russell Marion Dugdale

Follow this and additional works at: [https://digitalcommons.mtech.edu/bach\\_theses](https://digitalcommons.mtech.edu/bach_theses)



Part of the [Metallurgy Commons](#)

---

SYNTHETIC MANGANESE DIOXIDE PRODUCTION

---

A Thesis

Submitted to

Department of Metallurgy

Montana School of Mines

---

In Partial Fulfillment

of the Requirements for the Degree

Bachelor of Science

---

by

Russell Marion Dugdale

May 1956

SYNTHETIC MANGANESE DIOXIDE PRODUCTION

---

A Thesis

Submitted to

Department of Metallurgy

Montana School of Mines

27 71 4

---

In Partial Fulfillment

of the Requirements for the Degree

Bachelor of Science

---

by

Russell Marion Dugdale

May 1956

## TABLE OF CONTENTS

CHAPTER	PAGE
I. REVIEW OF PREVIOUS WORK . . . . .	1
Method of X-Ray Analysis . . . . .	9
II. THE PROBLEM . . . . .	11
III. PRODUCTION OF SYNTHETIC MANGANESE DIOXIDE . . . . .	13
Reagents . . . . .	14
IV. EXPERIMENTAL PROCEDURE USING HAYES X-RAY APPARATUS . . . . .	15
V. PHILLIPS X-RAY DIFFRACTOMETER . . . . .	16
VI. PRODUCTION OF PHILLIPS ADAPTOR UNIT FOR HAYES CAMERA . . . . .	17
The Stand . . . . .	19
Stand legs . . . . .	19
Collimator Tube . . . . .	21
Fixtures . . . . .	22
Horizontal adjustment fixture . . . . .	22
Vertical adjustment fixture . . . . .	22
Steadying and centering fixture . . . . .	23
VII. EXPERIMENTAL TECHNIQUE . . . . .	25
VIII. CONCLUSIONS AND RECOMMENDATIONS . . . . .	32
BIBLIOGRAPHY . . . . .	34
ACKNOWLEDGMENTS . . . . .	36

## LIST OF TABLES

TABLE	PAGE
I. Calculated d Spacings of the Experimental Sample .	25
II. Fleischer and Richmond - d Spacings for Cryptomelane . . . . .	26
III. Butler and Thirsk - d Spacings for Cryptomelane .	26
IV. High d Spacings Obtained by Dilution and Small Collimator . . . . .	28
V. First Set of Seeded Samples - d Spacings . . . .	29
VI. Second Set of Seeded Samples - d Spacings . . . .	30

LIST OF FIGURES

FIGURE	PAGE
1. Hayes X-Ray Camera and Phillips Adaptor Unit . . .	18
2. The Stand . . . . .	20
3. Steadying and Centering Fixture . . . . .	20

## CHAPTER I

### REVIEW OF PREVIOUS WORK

Before World War I the United States procured all of its battery grade manganese dioxide from the Caucasus. Even at this time some experimentation was under way to produce this depolarizing substance synthetically and the experiments were successful to a large extent so that when the ore from the Caucasus was cut off, the necessary material was produced synthetically. The shortage was relieved when a deposit of manganese dioxide was discovered in Montana, which was superior to the ore from the Caucasus. In the early 1920s, a deposit was found in the African Gold Coast which was far superior to both the Caucasian and the Montana ores.<sup>1</sup>

Some manganese ores are far superior to similar ores in the manufacture of dry cells. The reason for this difference is difficult to determine because of the similarity in appearance, chemical analysis, hardness, color and other properties. Research concerning these ores has been directed to the consideration that if the characteristic properties and peculiarities of the known ores could be determined, new ores could possibly be classified with these facts as criteria

---

<sup>1</sup>Phillip H. Delano, "Classification of Manganese Dioxides," Ind. and Eng. Chem., Vol. 42, Pt. 1, Jan.-June, 1950.

and new methods of production could be formulated for synthetic ores with the desired properties.<sup>2</sup>

Manganese dioxide exists in three crystalline allotropic forms which are pyrolusite, cryptomelane, and ramsdellite. There is some confusion as to terms referring to these oxides. The terms are redefined as follows: The term alpha refers to cryptomelane, beta to pyrolusite, and gamma to ramsdellite. The imperfectly crystallized minerals, showing a more or less incomplete x-ray pattern, which have been generally called gamma manganese dioxide, are really impure varieties of ramsdellite or pyrolusite. There is a series of patterns of infinite gradations between ramsdellite and pyrolusite. Ramsdellite and pyrolusite are known in the form of 100% manganese dioxide crystals, but gamma manganese dioxide, delta manganese dioxide, and cryptomelane retain various impurities. The cryptomelane group comprises a series of alkali compounds between  $Mn_8O_{16}$  and  $K_2 MnO_{16}$ .<sup>3</sup>

A whole series of compounds has been found to exist between ramsdellite and pyrolusite. Ramsdellite and pyrolusite are well crystallized and the members in between have

---

<sup>2</sup>W. F. Cole, A. D. Wadsley and Allan Walkley, Trans. Elec. Chem. Soc., Vol. 92, p. 133 ff.

<sup>3</sup>Ibid., p. 525.



varying degrees of crystallinity. In fact, there are so many intermediate types that any distinction in them must be arbitrary. Another difficulty experienced in classifying these ores is that some of them are complex mixtures of several oxides and the individual patterns are difficult to determine.<sup>4</sup>

There is no sharp line of demarcation between the various members of the series between ramsdellite and pyrolusite and between these members lies a continuous series consisting of active depolarizers which are impure, but homogeneous substances with distorted lattices. To name this large number of substances would be nearly impossible, so the term gamma manganese is used to refer to any poorly crystallized manganese dioxide mineral based on the ramsdellite pattern and usually characterized by the presence of the x-ray diffraction line at  $d_{hkl}$  equal 4.<sup>5</sup>

Cryptomelane has been found in nature and has been prepared in several ways. Different samples vary widely in composition but the x-ray pattern is essentially constant.

Many entirely different types of reactions produce cryptomelane patterns. Identical diffraction patterns cannot be trusted to prove the exact type, because the oxide may have

---

<sup>4</sup>Ibid.

<sup>5</sup>Ibid., p. 526.

a definite space lattice arrangement but vary in chemical composition. These varying properties will also cause the properties of batteries made from this material to vary. In all of these different compositions, the alkali is chemically bound and partly water insoluble. These high alkali members can be leached with water and a portion of the alkali will be removed, but the x-ray pattern does not change.<sup>6</sup>

Of all of the different methods used to classify the various properties of the manganese dioxide minerals, probably the most effective is x-ray diffraction. X-ray analysis allows classification of the different types of ores and predictions can be made as to their ultimate behavior from this classification. One very difficult property to determine in this type of material is the activity which it may have. This property can only be determined by actually making a battery utilizing the material in question and thereby testing its performance. This test is necessary because two samples of ore may produce the same x-ray pattern and exhibit entirely different properties when in service. The actual test is essential before the ore can be fully evaluated, but the x-ray studies give good indications as to the likelihood of an ore being an effective depolarizer.<sup>7</sup>

---

<sup>6</sup>Ibid.

<sup>7</sup>Delano, loc. cit.

The different oxides of manganese are classified by their crystalline structure as determined by x-ray or electron diffraction patterns. Even when classified in this manner there are apt to be secondary modifications within one crystalline species which might be of importance in determining certain features of dry cell behavior. These secondary modifications might be expected to arise as a result of lattice imperfections which could result as a function of surface area. The differences might also arise as a result of defects caused by lattice disorder, by non-stoichiometric composition, or by a combination of the two. These modifications manifest themselves when the particles are small. Classification by x-ray or electron diffraction is essential before the importance of these other effects can be measured.<sup>8</sup>

The depolarizing action of the manganese dioxides depends in part on the crystallinity of the material used. Amorphous types of material, or the less crystalline forms of the oxide, provide the better characteristics for a battery if it is to be used for short life and high drain applications. If the oxide used is more crystalline, then the life of the battery is good for low drain applications and long shelf life. It has been determined that ramsdellite is the type

---

<sup>8</sup>Cole, Wadsley and Walkley, loc. cit.

best suited for high drain applications with short life, and that cryptomelane, whose crystallinity is more pronounced than that of ramsdellite, is better suited for long shelf life and low drain applications. The proposed explanation of this behavior is that the more amorphous the depolarizer, the more surface area exposed to the electrolyte and metallic oxides that are formed by action of the electrolyte with the container. This results in the using up of the depolarizer very fast in the case of the more amorphous material, while the more crystalline material, which does not present as large a surface area, does not react as fast and, therefore, exhibits a much longer shelf life.<sup>9</sup>

This report will concern itself with types of manganese dioxide that are prepared commercially. One oxide upon which all of the investigators agree as to positive identity is the dense black oxide obtained when manganese nitrate is heated. This is the only manganese dioxide mineral that can be prepared in a pure enough state to be used as a standard in the determination of physical and chemical constants.<sup>10</sup>

It is not possible to prepare pure oxides of other varieties of manganese dioxide, on a reproducible basis,

---

<sup>9</sup>W. C. Whalen, U. S. Bureau of Mines Publication, 1910-1940, B-173, Chptr. 2, pp. 15-20.

<sup>10</sup>Cole, Wadsley and Walkley, loc. cit.

by wet methods. One time a precipitation may produce a particular type of oxide and the next precipitation conducted in the same manner with identical materials and conditions may produce a totally different type of oxide or a mixture of oxides.<sup>11</sup> It has been found that even with the aid of diffraction patterns, it is still necessary to confirm the results with a chemical test because some of the minerals are isostructural, such as cryptomelane, hollandite, and coronadite.<sup>12</sup>

Oxides which have the same x-ray pattern may differ in chemical properties. In one set of samples prepared by Glemser the numerical composition varied considerably, the "n" in the formula  $MnO_n$  being 1.93, 1.84, and 1.76. When the samples were boiled in nitric acid, the patterns were sharper but otherwise unchanged, and "n" had increased to 1.97 in each instance.<sup>13</sup>

Many of these manganese dioxide minerals contain additional elements.

The formula for cryptomelane is given as  $KR_8O_{16}$ . R is largely  $Mn^{IV}$ , but enough is of a lower valence to provide the need of a potassium atom. The composition is not completely uniform, the relative amounts of K and

---

<sup>11</sup>Ibid.

<sup>12</sup>Ibid.

<sup>13</sup>Ibid.

R varying to some slight degree. Also the K may be replaced by Na.<sup>14</sup>

Another verification of the fact that various products may result from the preparation of these oxides is the result of Gruner's experimentation:

Gruner stated that the precipitate obtained on adding HCl to boiling  $\text{KMnO}_4$  solution and neutralizing with ammonia was amorphous, but that it gave cryptomelane when heated to  $400^\circ\text{C}$ . Exactly the same result was obtained from the amorphous material formed by the addition of  $\text{KClO}_3$  to pure  $\text{Mn}(\text{NO}_3)_2$  in  $\text{HNO}_3$ . On repeating the latter experiment, however, a pyrolusite was formed in place of the amorphous material, and Gruner expressed the view that there was no way of predicting which oxide would be produced.<sup>15</sup>

Most of the samples studied by McMurdie were of commercial origin, the methods of preparation not being stated. They consisted chiefly of cryptomelane, delta  $\text{MnO}_2$ , and pyrolusite. One oxide prepared by slowly adding HCl to a hot solution of  $\text{KMnO}_4$  gave the pattern of delta  $\text{MnO}_2$  (cryptomelane). He also examined some natural ores including some of battery grade from the Gold Coast and from Montana.<sup>16</sup> McMurdie's conclusions were, as quoted by Cole, et al:

In addition to x-ray diffraction, McMurdie used electron diffraction and electron microscopy as aids

---

<sup>14</sup>Howard J. McMurdie, "Microscopic and Diffraction Studies on Dry Cells and Their Raw Materials," Trans. Elec. Chem. Soc., Vol. 86, 1944, p. 315.

<sup>15</sup>Cole, Wadsley and Walkley, op. cit., p. 135.

<sup>16</sup>Ibid.

in his examination. He was able to show from electron micrographs that within any one crystal species a wide variety of shapes occurred, and that electron diffraction patterns were more informative for some of the finest oxides.<sup>17</sup>

#### METHOD OF X-RAY ANALYSIS

W. F. Cole used the following procedure in his x-ray work:

The samples were diluted with collodion dissolved in acetone and prepared in the form of a rod 0.6 mm. in diameter in a special moulding unit. Exposures were made with filtered Fe radiation in cameras of radius 2.865 cm. With 1.0 mm. pinholes suitable exposures were obtained in 3 hours at 5 milliamp., 40 kilovolt peak. When cryptomelane samples were exposed, 0.5 mm. pinholes were frequently used so as to give clearer patterns of the high spacing region.

Initially film measurements were made to identify the characteristic patterns of each form of oxide, but once this had been done it was found possible to recognize readily the constituents of each sample by comparing its pattern with those of pure minerals.

In identifying the various oxides, extensive use was made of the literature already cited and to the American Society for Testing Materials' file for additional information.<sup>18</sup>

McMurdie used the following method in his x-ray diffraction work:

X-ray diffraction patterns were made on unfractionated samples of  $MnO_2$ , using cylindrical cameras of about 57 mm. radius and unfiltered Fe radiation. The samples were

---

<sup>17</sup>Ibid., p. 136.

<sup>18</sup>Ibid.

mounted on small glass rods. Comparison was made with patterns of known natural minerals obtained from the United States National Museum and the United States Geological Survey. Since these oxides contain much very fine material and since particles less than about 0.1 micron do not give good x-ray patterns, electron diffraction patterns were made on the fine fraction of most samples.

X-ray patterns of the zinc salts were made in cylindrical cameras having a radius of about 57 mm. Cu K alpha radiation was used. The optical properties were determined with a petrographic microscope.<sup>19</sup>

Modifications of these procedures were used in this work.

---

<sup>19</sup>McMurdie, op. cit., p. 314.



## CHAPTER II

### THE PROBLEM

Production of the same product consistently is the problem of the investigators in the production of artificial manganese dioxide. As has been previously stated, a precipitate may be formed of one specific crystal type by a specific process. In all other cases, if duplication was attempted by following the same procedure, a different crystal type or several crystal types may be produced in the same precipitation, whereas in the previous precipitation only one significant crystal specie was produced. Along with the difficulty of preparing any substance in one of its less stable forms, there is the possibility of a small amount of the original material being present during hydrolysis, and inducing the formation of its own crystal type by a seeding action.<sup>1</sup> There is a possibility of using this "seeding" action as a control over the type of precipitate produced, and this work will be directed to that end.

Cryptomelane was chosen to be used as a "seeding" standard. Reports by the references examined stated that

---

<sup>1</sup>Cole, Wadsley and Walkley, "X-Ray Diffraction Study of Manganese Dioxide," Trans. Elec. Chem. Soc., Vol. 92, 1947, p. 140.

cryptomelane is easily reproduced in a pure state. This type of crystal can then be used to insure the production of just one crystal specie in seeding reactions. If cryptomelane and ramsdellite could be produced separately, and in their pure state, batteries could be made to order, and no element of chance would prevail as to the manner in which the batteries would operate upon fabrication.

## CHAPTER III

### PRODUCTION OF SYNTHETIC MANGANESE DIOXIDE

Butler and Thirsk reported that alpha manganese, or cryptomelane, could be consistently produced by the method they used. The cryptomelane is of one crystal type and can be definitely identified by x-ray diffraction patterns.<sup>1</sup> They used the method of Selwood, Eischens, Ellis and Wethington to prepare cryptomelane, which is as follows: Put 36 gm. of manganous sulphate with 24 gm.  $\text{KNO}_3$  in 2.5 liters  $\text{H}_2\text{O}$ , and heat to boiling. Add approximately 1 liter 2%  $\text{KMnO}_4$  or until the solution acquires a pink color. Decant supernatant liquid and wash three to four times with 3-1 portions of water. Filter through asbestos and wash free of sulphate. Dry the brown product for 2 days at  $60^\circ\text{C}$ . Butler and Thirsk changed the procedure by adding a considerable excess of  $\text{KMnO}_4$  which they claim insures the production of cryptomelane.<sup>2</sup>

The modified procedure of Butler and Thirsk was used as cited except that the amounts of reagents were reduced as follows:

---

<sup>1</sup>G. Butler and H. R. Thirsk, "Structural Properties of Some Synthetically Prepared Manganese Dioxides," Elec. Chem. Soc. Journal, Vol. 100, 1953, p. 298.

<sup>2</sup>P. W. Selwood, R. R. Eischens, Marilyn Ellis and Kathryn Wethington, Amer. Chem. Soc. Journal, Vol. 71, p. 3040.

## REAGENTS

AS CITED24 gm  $\text{KNO}_3$ 36 gm  $\text{MnSO}_4$ 2.5 liters  $\text{H}_2\text{O}$ Add  $\text{KMnO}_4$  till pink.AS USED1.37 gm  $\text{KNO}_3$ 3.864 gm  $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$ 221 ml  $\text{H}_2\text{O}$ 2.72 gm  $\text{KMnO}_4$  (con-  
siderable excess)

Several samples were made following the described procedure and dried at  $60^\circ\text{C}$  for two days. The samples were then ground to minus 300-mesh in size in preparation for the x-ray work.

## CHAPTER IV

### EXPERIMENTAL PROCEDURE USING HAYES X-RAY APPARATUS

For x-ray work the samples of manganese dioxide were mixed with equal parts of starch. The samples were sealed in a glass capillary and x-ray diffraction patterns were taken with Cu radiation, the best available, on the Hayes X-Ray Apparatus. Two cameras were available which were of 7 cm. radius, but of different depths. The alignment of the small camera was off and the x-ray beam did not center on the sample. Neither lines nor fluorescence was obtained, with exposure times to six hours. Since the alignment of the little camera could not easily be corrected, the larger camera was tried and a film produced. In spite of various exposure times, the films were so dark that all except the very strong lines were blacked out and the film was useless. The patterns obtained were of no value.

## CHAPTER V

### PHILLIPS X-RAY DIFFRACTOMETER

A discussion of the results obtained in the experimentation with the Hayes unit brought forth the conclusion that an attempt should be made to produce a pattern on the Phillips diffractometer, since the Phillips Apparatus is equipped with an Fe tube. Fe radiation is the proper radiation for analysis of manganese materials.

A chart was produced on the Phillips Diffractometer between the  $2\theta$  angles of  $78^\circ$  and  $8^\circ$ . The important lines on the chart were not of sufficient intensity to produce positive identification, so it was decided to build a stand to adapt the Hayes camera for use on the Phillips X-Ray Apparatus.

## CHAPTER VI

### PRODUCTION OF PHILLIPS ADAPTOR UNIT FOR HAYES CAMERA

A collimator tube was produced to fit in the large tube in the Hayes Camera. Work was then begun on the stand which was to hold the camera. The stand (Fig. 1) was produced and put into operation, but after several trials it was found that the stand was unsteady and produced very weak patterns and little fluorescence. A fixture was made which could be used to center and steady the camera, and hold a strict alignment. It was bolted to the top of the Phillips Apparatus.

The camera was set up, centered and aligned, and a sample and film placed in it. A running time of 3 hours was tried. Little success was met and longer exposure times were tried. Definite lines were produced but none of them correlated with anything in the literature, so once again a complete check was started to find what was disturbing the functioning of the camera. The horizontal and vertical alignment was off and it was necessary to raise the camera in order to get the full power of the x-ray beams on the sample. The largest pinhole available (0.040-0.060) was put in the collimator tube to afford the strongest beam possible

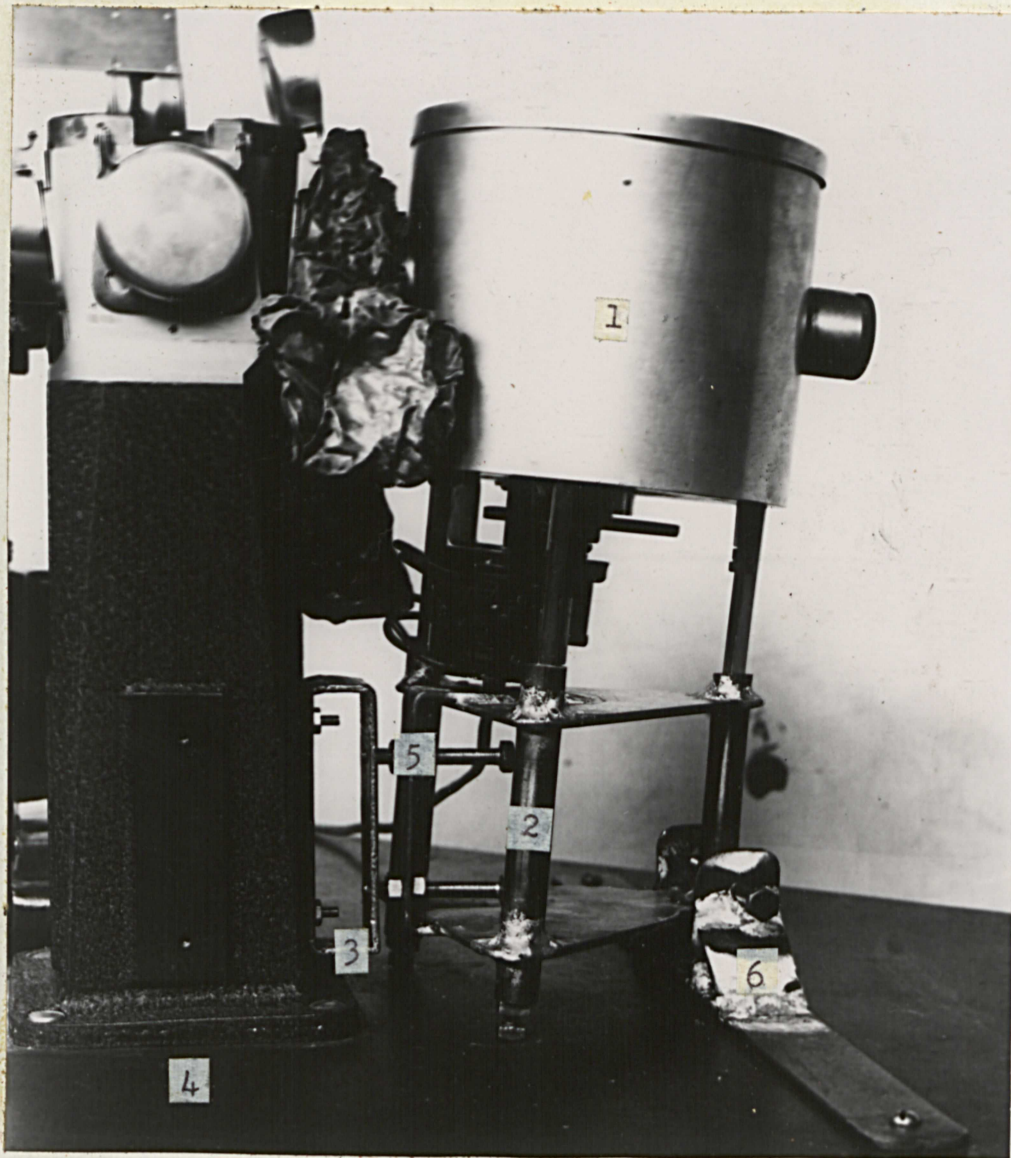


FIGURE I

## HAYES X-RAY CAMERA AND PHILLIPS ADAPTOR UNIT

- |                        |                                       |
|------------------------|---------------------------------------|
| 1. Hayes X-Ray Camera  | 4. Phillips X-Ray Unit                |
| 2. Stand Legs          | 5. Vertical Adjustment Fixture        |
| 3. Rectangular Fixture | 6. Steadying and Centering<br>Fixture |



on the sample. The next exposure produced positive results and further experimentation was directed to solving the problem.

### THE STAND

The proposed adaptor unit would necessarily have to be solid so that it could not be easily jarred out of alignment, and so that the camera (Fig. 1, No. 1) could be easily taken from the stand (Fig. 2) and just as easily replaced. It was decided that the stand would be made of heavy metal and all of the pieces would be welded or bolted together.

### STAND LEGS

A piece of low carbon steel  $5/8$  in. in diameter was used to make the stand legs (Fig. 1, No. 2). The material was turned down in a lathe until the piece was smooth. The legs were then cut to length and the ends turned. An increase in height of 4.5 in. was needed. This increase, with an allowance for height adjustment, was provided by bolts threaded in the bottoms of the legs. The bolts have locknuts on them to secure the bolts once the stand is properly adjusted. A  $3/8$  in. hole  $3/4$  in. deep was bored in the top of each stand leg. These holes were large enough to permit the legs of the camera to fit into them. The rear leg of the camera is

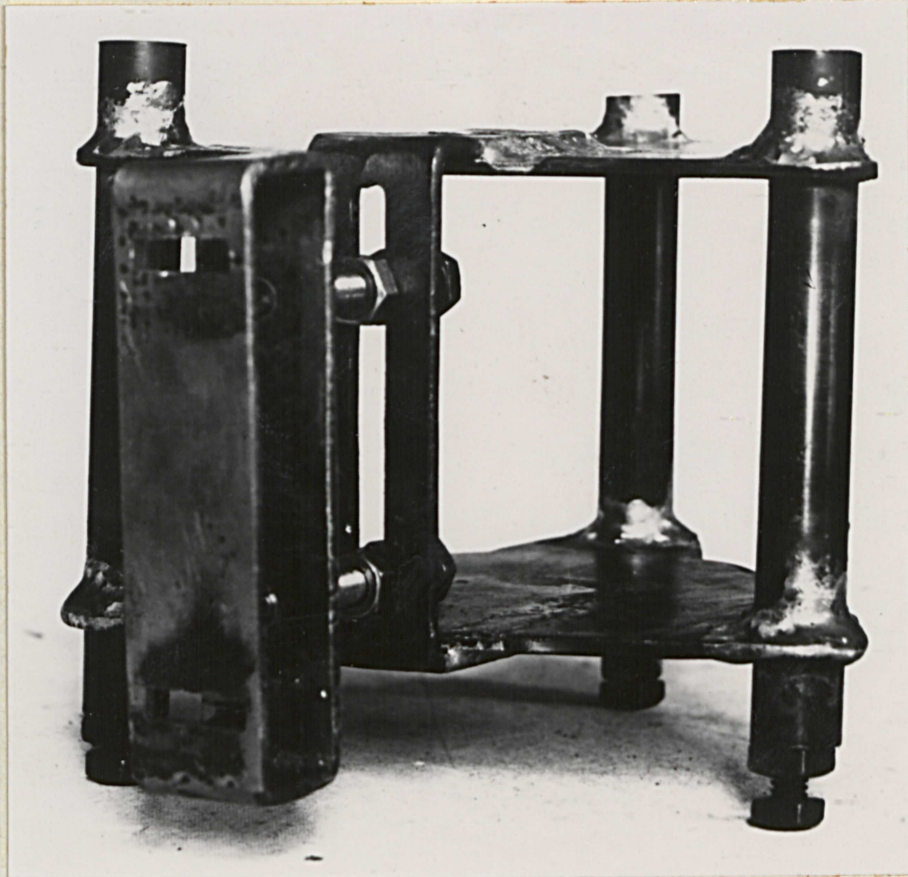


FIGURE 2 - THE STAND

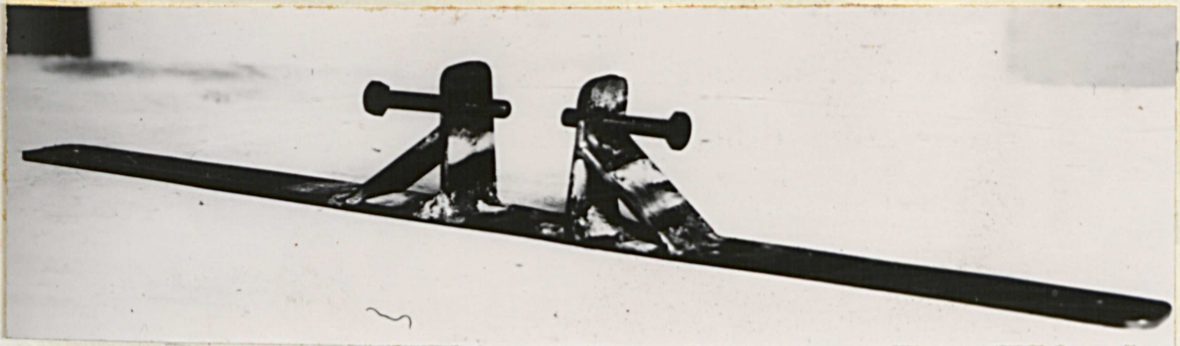


FIGURE 3 - STEADYING AND CENTERING FIXTURE

shorter than the front legs because the x-rays emanate from the apparatus at an angle and the short rear leg provided the angle.

The two horizontal plates were made by drilling three holes in two  $1/8$  in. triangular plates. These holes were  $5/8$  in. in diameter and just large enough to accommodate the stand legs. The stand legs were placed on the camera and the lower plate was put into position and welded to the legs. After some minor adjustments, the upper plate was welded into place thereby affording a good solid stand on which to place the camera.

#### COLLIMATOR TUBE

Originally the Hayes camera was affixed to the Hayes X-ray unit by means of a projection from the vertical post on the Hayes unit. This projection is tapered slightly and fits snugly into a female tube on the camera.

This projection holds a collimator which serves to align the x-ray beam on the pinhole, which in turn aligns the x-rays on the sample.

A piece identical to the projection was turned on the lathe. The projection has the collimator fitted in it and the camera is then butted against the window of the x-ray tube.

## FIXTURES

Affixing the stand to the vertical post of the Phillips X-Ray Apparatus was the next problem. The attachment fixtures had to allow horizontal and vertical adjustment of the camera stand.

## HORIZONTAL ADJUSTMENT FIXTURE

A rectangular fixture (Fig. 1, No. 3) was fabricated to provide horizontal adjustment. This fixture has two horizontal slots  $1/8$  in. wide and 1 in. long and 3.15 in. apart. Horizontal adjustment was provided by these slots which were cut in one side of the rectangular fixture. The slots fit over the machine-screw studs which were threaded into the vertical post of the Phillips unit (Fig. 1, No. 4).

## VERTICAL ADJUSTMENT FIXTURE

The vertical adjustment fixture (Fig. 1, No. 5) was made in the form of a blocked-U in which the legs of the U were 3.15 in. apart. A slot,  $1/4$  in. wide and 3 in. long, was cut in the vertical section of the U and the fixture was welded onto the camera stand after it had been properly oriented.

Holes were drilled in the rectangular fixture and tapped to accommodate  $1/4$  in. bolts. The stand was placed

in position and the 1/4 in. bolts were put through the vertical slot and turned into the tapped holes on the rectangular fitting. A nut was provided on either side of the vertical slot to allow movement of the camera along its principal axis. This slot allows vertical adjustment of the camera. When the camera is finally oriented in the proper manner, the nuts are tightened on both sides of the slot, thereby restricting both vertical and horizontal motion.

#### STEADYING AND CENTERING FIXTURE

It was found that the camera had some horizontal motion because the rear leg of the stand was so far from the vertical post of the x-ray unit. A steadying and centering fixture (Fig. 1, No. 6 and Fig. 3) was needed to restrict this motion.

The top of the Phillips X-Ray Apparatus has holes in it so that shields can be set up at  $90^{\circ}$  intervals. These holes are in line with the leg of the camera stand that is furthest from the vertical post of the x-ray unit.

Holes were drilled in a piece of strap iron so they would match the holes in the top of the x-ray apparatus. Two vertical pieces of strap iron were welded to the horizontal strap and braces were then welded to the vertical straps at

an angle so they extended away from the rear leg of the camera support. Holes were drilled in the vertical projections and tapped to accommodate bolts which would bear on the rear camera leg and provide the alignment required. A hole was cut in the horizontal strap to accommodate the rear leg of the camera stand and yet allow freedom of movement so the optimum alignment of the camera could be obtained.

## CHAPTER VII

### EXPERIMENTAL TECHNIQUE

The first two samples were produced, dried, ground, diluted 1 to 1 with starch and sealed in glass capillaries. They were placed in the Hayes Camera and a diffraction pattern taken. All patterns were produced with a camera of 7 cm. radius with a 0.040 in. collimator, at 30 Kv and 10 Ma and an exposure time of 3 hours.

The diffraction patterns of the four samples were identical so a representative one was examined and the d spacings calculated. The results of these calculations are as follows:

d	I ( Estimated)	d	I (Estimated)
3.650	7	1.5321	7
3.270	5	1.5020	4
2.976	6	1.4809	3
2.933	10	1.4557	7
2.864	4	1.3861	8
2.648	5	1.2286	7
2.350	5	1.1923	7
2.1373	9	1.1319	2
2.0830	4	1.1158	2
1.8703	6	1.0987	2
1.7711	7	1.0877	2
1.7242	7		

The material described above was supposed to be cryptomelane and d spacings for cryptomelane were taken from the literature.

Fleischer and associates reported the following:<sup>1</sup>

d	I	d	I	d	I
6.863	9	2.097	1	1.385	0.5
4.892	8	1.961	1	1.347	5
3.105	10	1.820	5	1.230	0.5
2.445	3	1.633	4	1.209	0.5
2.387	7	1.618	4	1.190	0.5
2.305	1	1.544	1	1.135	0.5
2.183	4	1.528	6	1.073	1
2.145	5	1.423	2	1.052	1

The d spacings and intensities for cryptomelane are:<sup>2</sup>

d	I	d	I	d	I	d	I
7.03	S	3.12	MSvd	1.826	Wd	1.424	W
4.94	M	2.401	Svd	1.539	Wd	1.355	VWd
3.49	VWd	2.150	Md				

<sup>1</sup>Michael Fleischer and Wallace E. Richmond, "The Manganese Oxide Minerals: A Preliminary Report," Economic Geology and the Bulletin of the Society of Economic Geologists, Vol. 38, June-July, 1943, No. 4, p. 281.

<sup>2</sup>G. Butler and H. R. Thirsk, "Structural Properties of Some Synthetically Prepared Manganese Dioxides," Elec. Chem. Soc. Journal, Vol. 100, 1953, p. 299.



The strongest lines reported above are: The strongest at 7.07 and 3.105; next strongest at 6.863 and 2.401; and third strongest at 4.892 and 3.12. The diffraction patterns produced did not match either of the patterns quoted, and the high d spacings were not visible because of fluorescence.

A search of the literature produced a reference that stated that the higher d spacings could be obtained if an 0.020 in. collimator were used.<sup>3</sup>

A smaller collimator (0.025 in.) was used and very light patterns were obtained with 4 hour exposures. Even with the increased exposure time, the high d spacing lines were barely discernible although the lines were less diffuse. It was then decided that if the samples were diluted more with starch that less fluorescence would be obtained and that if the lines were present they could be more easily seen. The 0.030 in. collimator was used throughout the remainder of the experiment because the 0.025 collimator required too much time to obtain a diffraction pattern.

A sample was diluted 2 to 1 with starch and a diffraction pattern obtained which is as follows:

---

<sup>3</sup>Cole, Wadsley and Walkley, "X-Ray Diffraction on Study of Manganese Dioxide," Trans. of Elec. Chem. Soc., Vol. 92, 1947, p. 136.

d	I (Estimated)	d	I (Estimated)
7.13	9	2.44	8
5.19	10	2.25	7
3.66	3	2.14	7
3.02	6	2.04	2

These new patterns of the original samples prove that with more dilution and a small collimator the high d spacings can be obtained.

The results of the experimentation are not conclusive because the experimental samples could not be definitely identified. Since the experimental procedure was designed to produce cryptomelane, the references cited for d spacings are limited to those for cryptomelane. All obtainable diffraction patterns of manganese oxides other than cryptomelane were examined but none of these matched the patterns of the experimental sample.

More samples were produced using the material produced in the first set of samples as seed. The method used to produce this material was essentially the same as that used to prepare the first set of samples, except that a little of the seed material was ground to minus 300-mesh in size and added prior to precipitation. Also, in the precipitation process, only enough  $\text{KMnO}_4$  was added to turn the solution pink.

The four samples produced in this manner were x-rayed

and a diffraction pattern obtained using the same x-ray procedure as above, except that a 4 hour exposure time was used.

The first two samples precipitated produced identical patterns, as did the third and fourth samples. The material produced in the first and second samples was far different from that produced in the third and fourth samples. A check of the procedure uncovered the fact that the operator was called away in the middle of the filtering operation after the first two samples were filtered. They were filtered immediately after precipitation. The last two samples remained in the mother liquor for an hour after precipitation and the temperature of the mother liquor dropped to that of room temperature during the delay.

Each set of the two sets of samples produced essentially the same diffraction patterns although the two sets differed considerably in that the first set of samples produced more lines than the second, and the d spacings differed.

FIRST SET OF SEEDED SAMPLES - D SPACINGS

d	I (Est.)	d	I (Est.)	d	I (Est.)	d	I (Est.)
7.03*	8	3.11	6	2.044	5	1.55*	3
5.19*	9	2.425*	10	1.632*	3	1.428	4
4.17	3	2.132*	7				

\* Average of both films.

## SECOND SET OF SEEDED SAMPLES - D SPACINGS

d	I (Est.)	d	I (Est.)
5.21*	10	2.48*	9
4.04	2	2.14*	8
3.15	2	1.93	4
3.035	2		

\* Average of the two films.

A comparison between the two sets of seeded samples shows several points of comparison and the two sets of samples are essentially the same except for the absence of the line at 7 angstroms in the second set. These d values compare favorably with those stated by Butler and Thirsk although they do not match exactly.

Nearly all of the lines produced were diffuse, so measurement was difficult and a high degree of accuracy in measuring the lines was not obtained. A definite evaluation of the material produced was not possible within the time limits of this thesis.

There is a possibility that the line produced at the d of 7 could have been caused by the presence of some asbestos in the samples. Asbestos was used as a filter medium as recommended in the literature. Future work on this problem should be done in some manner that will avoid the carry-over

of unwanted material into the sample. A sintered glass filter would meet this specification and thereby rule out the possibility of asbestos producing this line at 7 angstroms on the diffraction patterns.

## CHAPTER VIII

### CONCLUSIONS AND RECOMMENDATIONS

Although the results are not conclusive as to the type of manganese dioxide produced, they do prove that the material can be reproducibly produced, at least with the few diffraction patterns obtained in this experiment as proof of this point. These patterns do not produce decisive evidence but they do give a strong indication that this particular manganese dioxide material can be reproducibly produced. Seeding reactions are possible as indicated by the x-ray diffraction patterns of the seeded material. The results are limited in scope and no definite statement can be made. The results indicate that the seeding reaction will work but further investigation will be necessary to confirm this possibility.

During the course of the investigation, it was found that Cu radiation is totally unsuited for the production of diffraction patterns of  $MnO_2$ ; the  $MnO_2$  is so amorphous that a conclusive diffraction pattern cannot be produced on the Phillips diffractometer.

Well defined films can be produced with the Hayes Camera on the Phillips X-Ray Apparatus using Fe radiation, with a setting of 30 Kv-10 Ma, and an exposure time of 4 hours.

Choice of the proper collimator to use will depend on the individual sample being investigated, but it is suggested small collimators in the range from 0.020 in. to 0.030 in. be used in the investigation of the more amorphous types of material, such as manganese dioxide.

Upon occasion the alignment of the camera should be checked by use of the fluorescent screen in order to insure the strongest beam of x-rays possible on the sample.

Care should be taken to put a piece of lead foil over the collimator tube when the camera is butted against the Phillips x-ray unit to prevent radiation leaks. No radiation was observed upon checking, but the possibility of irradiation should not be overlooked. Another safety precaution is that the camera be removed from the stand only when the x-ray unit is turned off. Also, the cover should be put in place over the aperture through which the x-rays emerge when the camera is removed from the stand.

BIBLIOGRAPHY



## BIBLIOGRAPHICAL ENTRIES

- Butler, G. and H. R. Thirsk. "Structural Properties of Some Synthetically Prepared Manganese Dioxides." Electrical Chemical Society Journal. Volume 100, 1953, pp. 297-301.
- Cahoon, N. C. "An Electrochemical Evaluation of Manganese Dioxide for Dry Battery Use." Electrochemical Society Journal. Volume 99, 1952, pp. 343-348.
- Cole, W. F., A. D. Wadsley and Allan Walkley. "An X-Ray Diffraction Study of Manganese Dioxide." Volume 92, 1947, Transactions of the Electrochemical Society, pp. 133-158.
- Delano, Phillip H. "Classification of Manganese Dioxides." Industrial and Engineering Chemistry. Volume 42, pt. 1, Jan-June 1950, pp. 523-527.
- Fleischer, Michael and Wallace E. Richmond. "The Manganese Oxide Minerals: A Preliminary Report." Economic Geology and the Bulletin of The Society of Economic Geologists, Volume 38, June-July, 1943, No. 4, pp. 269-286.
- Glicksman, Richard and C. K. Morehouse. "Resistivity Studies of Various Leclanche Cathode Materials." Journal of the Electrochemical Society. Volume 103, No. 3, March 1956, pp. 149-153.
- McMurdie, Howard F. "Microscopic and Diffraction Studies on Dry Cells and Their Raw Materials." Transactions of the Electrochemical Society. Volume 86, 1944, pp. 313-326.
- Moore, E. T., Marilyn Ellis and P. W. Selwood. "Solid Oxides and Hydroxides of Manganese." American Chemical Society. Volume 72, p. 856, 1950.
- Morehouse, C. K. and R. Glicksman. "A Technique for Evaluating Various Cathode Materials." Journal of the Electrochemical Society. Volume 103, No. 2, Feb. 1956, pp. 94-98.
- Selwood, P. W., R. R. Eischens, Marilyn Ellis, and Kathryn Wethington. "Disperse Structure of Manganese Oxides and a Magnetic Method for Studying Depolarizer Action in the Leclanche Cell." The American Chemical Society, Volume 71, pt. 2, July-Dec. 1949, pp. 3039-3040.

U. S. Bureau of Mines; Material Survey Manganese, III-9-Specs.; XVIII-40- "Manganese in Battery Industry"; Signal Corps-Specs-Military Battery Grade; S. C. L.; 3120-13, Oct. 10, 1949.

Whalen, R. C. U. S. Bureau of Mines Publications, 1910-1940, B-173. Chptr. 2, pp. 15-20.

## ACKNOWLEDGMENTS

The writer wishes to express his gratitude to Doctor Frederick A. Hames and Professor Ralph I. Smith, of the Metallurgy Department, for the kindness and understanding shown, as well as for the many valuable suggestions and criticisms tendered, without which the work could not have been completed. The suggestions concerning the writing of this paper by Doctor Frederick A. Hames and Professor Ralph I. Smith were greatly appreciated and especially the attention and energy devoted to correction and rewriting of the rough draft by Professor Ralph I. Smith.

Mr. Earl T. Denny, Campus Foreman, provided the material for use in this project, instructions in operating the lathe and in welding, and tools from the shop for the pursuit of this project, for which the writer is very grateful.

Mrs. Loretta B. Peck, Librarian and Assistant Professor, provided invaluable aid in the library research conducted on this thesis and her assistance is sincerely appreciated.

An expression of thanks is extended to all of my fellow students because of the help extended and interest shown during this project.