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HW--7-4063

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#1 D.A. Miller-T.N. Stapleton-M.H. Smith-700
 #2 J.N. Tilley - Wilmington
 #3 W.C. Kay - W.E. Jordan
 #4 C.N. Gross - 300
 #5 Area Engineer - Att: Patent Group
 #3 Area Engineer
 #7 C.P. Kidder
 #8 P.A. Dahlen
 #9 C.W.J. Wende
 #10 Extra Copy *W Parker*
 #11 Extra Copy
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FINAL REPORT

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PRODUCTION TEST 105-2-P (SUPPLEMENT A)

ACTIVITY OF PILE DISCHARGE WATER
(ACTIVATION OF MANGANESE AND IRON)

Classification Cancelled (Change to)

Declassified

Reference RLR-66-4

AE Lyden 2-12-5-40

B. G. G. 1/3/41

Leure 1/3/91

Prepared by

J. M. West
 100 Technical

MASTER

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May 8, 1946

FINAL REPORTPRODUCTION TEST 105-2-P (SUPPLEMENT A) - ACTIVITY OF PILE DISCHARGE WATER
(ACTIVATION OF MANGANESE AND IRON)Introduction

Previous studies of pile discharge water have shown that one of two processes is responsible for the large but variable amount of Mn^{56} (2.6 hr.) activity present in the water. These processes are:

- 1) Production of Mn^{56} by the reaction $Mn^{55}(n,\gamma)$ on manganese impurity in the water. The amount of such impurity has been shown to be too small to produce the observed amount of Mn^{56} unless the mean irradiation time is increased by a large factor due to temporary sticking of manganese on the surfaces in the tubes;
- 2) Production by the reaction $Fe^{56}(n,p)$ on iron in the film. The present production test was designed to determine which of these processes is responsible for the troublesome Mn^{56} activity and to what extent the activity is increased due to sticking of manganese or iron in the tubes.

Summary

The addition of 0.117 p.p.m. manganese to Tube No. 2469 at 100-F on March 28, produced additional Mn^{56} activity which increased in approximately an exponential manner with time. After 4-1/2 hours addition at constant concentration, the Mn^{56} component had increased from an initial value of 15 disintegrations/c.c./sec. to about 200 dis./c.c./sec.; which is 25 to 30 times the amount expected from cross section, flow rate, and flux density considerations. With this sticking factor only about 0.005 to 0.01 p.p.m. of manganese impurity are required to produce the 15 dis./c.c./sec. of Mn^{56} activity present in the water prior to the test.

The rate of increase of the Mn^{56} component while manganese was being added at constant concentration, and the rate of decrease after the addition stopped, indicate that the mean sticking time is about 45 minutes. Two percent of the manganese in the water, sticking for this length of time, could produce the effect observed.

The possibility that any significant part of the Mn^{56} activity in pile discharge water is due to the $Fe^{56}(n,p)$ reaction was eliminated on April 1, when 1.17 p.p.m. of iron were added to Tube No. 2465, at 100-F Area, for 8 hours. If any Mn^{56} at all was produced, the amount was too small to be measured under the prevailing conditions. Results of this test were confused by the presence of a large amount of copper [Cu^{63} (12.8 hr.) and Cu^{65} (5 min.)] activity in the water. This copper undoubtedly was picked up from the copper feeder line. If all of the unidentified activity is assumed to be Mn^{56} , the amount of this component which could be produced by 0.01 p.p.m. of iron in the water would not be greater than 2 or 3 percent of the total.

The pressure drop due to film in Tube No. 2465 increased from 7 p.s.i. to 51 p.s.i. due to the addition of 1 p.p.m. iron in the form of ferric nitrate for 8 hours. After the metal was discharged and replaced, the pressure drop was about 10 p.s.i.

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Details

Tubes 2465 and 2469 at 100-F Area were chosen for the tests because of their readiness for discharge on April 2, and because available pressure feeler lines could be used for adding chemical solutions and collecting outlet samples for analyses. A positive displacement pump of the type previously used to introduce UNH solution in Production Test 105-13-1, (Simulated Jacket Failure, IDS-70, January 4, 1945) was used to pump the solutions at a constant rate through the inlet feeler lines. An ionization chamber of the type used for water monitoring in the sample rooms was connected in the outlet feeler line. An Esterline Angus Recorder provided a continuous record of the water activity as it passed through the chamber. The relative sensitivity of the ionization chamber to the Mn^{56} component was increased by including a 12 liter holdup volume in the sampling line. The flow rate was adjusted to give a theoretical holdup time of about 25 minutes but the effective holdup time was only 10-15 minutes, (due to mixing in the holdup chamber) as evidenced by the premature appearance of activity in the chamber after increases in concentration of the additives.

Solutions of manganous sulfate ($MnSO_4 \cdot H_2O$) and ferric nitrate [$Fe(NO_3)_3 \cdot 9H_2O$] in various concentrations were prepared for the tests as specified in the Production Test. These compounds were considered suitable from the standpoint of purity and solubility. The addition of manganese was made to tube 2469, March 28 and that of iron was to tube 2465, April 1. The tests will first be considered separately.

I Manganese Activation

Two normal water samples were taken from the outlet of tube 2469 prior to the addition of manganese. The counting rate from a 150 c.c. portion of each sample was measured exactly 54 minutes after sampling. Evaporated samples of 5 c.c. each were also prepared for running decay curves. All measurements on subsequent samples were compared with these results to determine deviations from normal.

The first concentration of manganese was 0.00117 p.p.m. The pumping speed was 117 c.c./min. and remained constant throughout the manganese and iron addition tests. The first spot sample for counting was taken 35 min. after the pumping started. Other samples were taken at 10 minute intervals. The counting rate of a 150 c.c. portion of each sample was determined 54 minutes after sampling by placing a beaker under a thin mica window counter tube. Evaporated samples were prepared when measurements on 150 c.c. portions indicated significant changes in activity. The decay curves on these samples were analyzed graphically to obtain the amounts of the Mn^{56} (2.6 hr.) and Mn^{24} (14.8 hr.) components. The results of these measurements are shown in Figure I and Figure II. A slight increase in activity is apparent at 0.00117 p.p.m. concentration.

After 1 hr. at 0.00117 p.p.m., the pump was stopped momentarily before increasing the concentration to 0.00585 p.p.m., by increasing the strength of the feeder solution while maintaining a constant flow rate. Further increases occurred at this concentration. The activity apparently increased with time also, indicating that manganese was sticking in the tubes.

In order to obtain large, easily measured changes in activity, the concentration was increased to 0.117 p.p.m. where it remained constant for 4-1/2 hrs. Results of counting measurements on 150 c.c. samples are shown in Figure I. An increase by a factor of about 4.5 had occurred in the first sample, which was taken 35 minutes after the pump was started. The activity continued to increase.

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in approximately an exponential manner thereafter. At the end of 4-1/2 hours, saturation had not yet been reached, but the rate of increase was low. The addition of manganese was stopped suddenly at this time, and the decrease in activity as a function of time was measured for several hours.

The disintegration rates of Mn^{56} and Na^{24} , determined by graphically analyzing decay curves on evaporated samples, are shown in Figure 11. The thin mica window counter used for these measurements was calibrated with a uranium oxide source. The efficiency of the counter, for the geometry used, was found to be 26 percent.

In addition to the expected increase in Mn^{56} activity with increases in concentration, and with time at a given concentration, the Na^{24} component also appears to have increased slightly at 0.117 p.p.m. concentration. It is not known at present whether the increase in the 14.8 hr. component is real or whether the apparent increase was an inherent error. The higher disintegration rates were obtained on samples representing only 2 c.c. of evaporated water, while the lower ones were obtained on 5 c.c. portions. Impurities such as zinc (0.01%) may have produced additional activity of approximately the same half life as sodium. Some copper may have entered the solution from the copper feeder line, but the amount should have been slight, since the pH of the most concentrated feeder solution was about 8.2.

After 4-1/2 hours at 0.117 p.p.m., the disintegration rate of Mn^{56} was approximately 200 dis./c.c./sec. The disintegration rate prior to addition of manganese was about 15 dis./c.c./sec. The saturated value, based on the shape of the curve in Figure 1, would probably be 10-15 percent higher. If a saturation value of 225 dis./c.c./sec. is assumed, the ratio of the final activity produced by 0.117 p.p.m. manganese to that originally present in the water is 15 to 1. If the Mn^{56} activity is proportional to the manganese concentration in the water, the amount of manganese originally present in the water was 0.0078 p.p.m. The average increases in counting rates over the base values on the first 3 samples taken at 10 minute intervals at each concentration (the first sample was taken 35 min. after addition began, in each case) are 68, 313, and 2440 c.p.m. (Figure 1) at 0.00117, 0.00585, and 0.117 p.p.m. respectively. The relative increases per unit concentration are 1.0, 0.93, and 0.35. Since smaller concentrations appear to be more effective in increasing the Mn^{56} component, the original concentration of manganese in the water may have been as low as 0.003 p.p.m. The most reliable values reported from various chemical and spectroscopic tests range between 0.001 and 0.01 p.p.m.

The outlet temperature of tube 2469 was 37.5°C and the inlet temperature 7.5°C. The average nv in the metal can be calculated from the following relation: (Document number 7-3024, "Polonium Production", Dec. 3, 1945)

$$\Delta T = (6.86) (nv) (10^{-12})$$

$$nv = \frac{30}{6.86 \times 10^{-12}} = 4.4 \times 10^{12}$$

Using this value for the average nv in the water, together with the following constants, the expected disintegration rate of Mn^{56} is calculated.

Percent abundance of Mn^{55} = 100
 Cross Section of Mn^{55} = 11×10^{-24}
 Half life of Mn^{56} = 2.6 hrs.
 Transit time through tube = 1.6 sec.

$$0.117 \text{ p.p.m.} = 1.17 \times 10^{-7} \text{ gms./c.c.} = 1.3 \times 10^{15} \text{ atoms/c.c.} \quad -1.6$$

$$\text{Disintegration rate} = (1.3 \times 10^{15}) (11 \times 10^{-24}) (4.4 \times 10^{12}) (1.6) = 13800$$

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The ratio of the experimental disintegration rate to the theoretical one is 225/7.4. This indicates a sticking factor of about 30. Because of this large sticking factor, the very small amount of manganese impurity in the process water is sufficient to account for all of the Mn^{56} activity found in the pile discharge water.

The decrease of the additional Mn^{56} activity (amount above normal) as a function of time is shown in Figure III. The curve appears to be a sum of exponentials and can be analyzed reasonably well into a short and a long component of 28 min. and 6 hr. half lives. The period of the shorter component is indicative of the mean sticking time of the manganese on the surfaces before being washed away, as can be shown in the following manner:

Let A = total number of atoms of manganese sticking in the tube at any time t

N = number of active atoms of manganese sticking in tube

Assume that the number of atoms washed away per unit time is proportional to the number present = C_1A

and that the number of active atoms washed away per unit time = C_1N

Atoms sticking in the tube will become activated at a rate proportional to the number present = kA

The active atoms will decay at a rate proportional to the number of active atoms = LN

The rate of change of the total number of sticking manganese atoms can be expressed as

$$\frac{dA}{dt} = -C_1A$$

whose solution is $A = A_0 e^{-C_1t}$

where A_0 = number of atoms present at time $t = 0$

The rate of change of the active atoms in the film is

$$\frac{dN}{dt} = kA_0 e^{-C_1t} - LN - C_1N$$

The solution of the above linear equation is:

$$N = \frac{kA_0}{C_1} e^{-Lt} + \frac{(N_0 - kA_0)}{C_1 + L} e^{-(C_1 + L)t}$$

where N_0 = number of active atoms present at $t = 0$

The number of active atoms in the water is C_1N , and therefore, the disintegration rate will be proportional to C_1N

$$\text{Disintegration rate} = kA_0 e^{-Lt} + (N_0 - kA_0) e^{-(C_1 + L)t}$$

The disintegration rate as a function of time is therefore represented as a sum of exponentials having periods of $\frac{1}{L}$ and $\frac{1}{C_1 + L}$. The former is the

decay period of manganese (3.75 hrs.). Taking the experimental value of the shorter period (Figure III), the value of C_1 can be calculated as follows:

$$\text{Numerical value of } L = 0.0044 \text{ min.}^{-1}$$

$$\frac{1}{C_1 + L} = 28 \text{ min.}$$

$$C_1 = 0.0203 \text{ min.}^{-1}$$

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The mean sticking time ($\frac{1}{\bar{v}_1}$) of the manganese is therefore about 49 minutes.

Since a half life of 6 hours instead of 2.6 hours was obtained experimentally for the longer component, this value might be more significant in making an estimate of the mean sticking time. In this manner, a value of 44 minutes is obtained for the mean sticking factor. About 2 percent of the manganese sticking in the tubes for this length of time is sufficient to account for the large sticking factor observed.

Although a component of half life approximately 28 minutes seems to be definitely indicated, (Figure III) the analysis for longer components is rather arbitrary. Instead of a single 6 hr. component, the longer period can be represented equally well by two components of 2.6 hr. and 14.8 hr. half lives. This analysis has no significance except when considered together with the apparent small increase in the Na^{24} component during the manganese irradiation. The period of the shorter component is largely independent of the manner in which the longer periods are analyzed, and a value of 45 minutes is probably fairly accurate for the mean sticking time.

An increase of 1 p.s.i. over and above the average change in other pressure drop tubes at 100-F Area was measured in tube 2469 on the day following the test. The activity of the discharge water was normal 20 hours after completion of the test.

II Iron Activation

The same experimental procedure was followed in the addition of iron to Tube No. 2465 at 100-F April 1, as that previously used for the introduction of manganese. Only one concentration (1.17 ppm) was used for this test since it was felt that the source of the major part of the Mn^{56} activity had been determined in the previous test, and no measurable effects were expected at low concentrations of iron. Samples were collected in the same way as before. Counting rates were measured on 150c.c. samples of water 54 minutes after sampling, and decay curves were run on representative evaporated samples. Pressure and temperature measurements were taken periodically to determine the extent of film deposition.

The counting rates on 150c.c. samples are shown in Figure IV. The early results were confused by the necessity for stopping the pump twice because of leaky connections in the feeder line. A large increase in counting rate occurred soon after the addition began, followed by a rapid decrease which in turn was ultimately reversed, becoming a gradual increase which continued until the pump was stopped. The low rate of decrease after the addition was discontinued indicates that the mean sticking time of the component responsible for the increased activity was much longer than that previously observed for manganese.

The results obtained by graphically analyzing decay curves on samples taken during this test showed that the increase in activity was almost entirely due to two components of half lives 12.8 hours and approximately 5 minutes. A very small amount of activity of intermediate half life could not be resolved. It appeared to be a mixture of half lives. The two strong components were shown to be due to copper [Cu^{63} (12.8 hr.) and Cu^{65} (5 min.)]. This was determined by making a chemical separation of copper as the sulfide, measuring the half life, and showing that the measured activity of the 12.8 hr. component was

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entirely due to beta rays (Cu^{63} does not emit gamma rays). Concern was felt prior to the test over whether the concentrated ferric nitrate feeder solution would dissolve copper from the tube through which the solution was pumped. The pH of this solution was measured and found to be 2.0. When no attack was observed on a sample of copper placed in a portion of the solution, it was concluded that the amount of copper which might contaminate the solution would be small. The fact that copper sticks on surfaces to a great extent made even a minor amount of this impurity very troublesome, however. The test was continued in spite of this difficulty, because, although no accurate measure of the cross section of the reaction $\text{Fe}^{56}(\text{n},\text{p})$ was obtained, it was definitely shown that the contribution of iron to the amount of Mn^{56} in pile discharge water is relatively unimportant.

An upper limit to the amount of Mn^{56} produced from the iron is obtained by assuming all of the unidentified activity resulting from graphical analyses of decay curves to be Mn^{56} . The maximum amount of this activity was about 20 dis./cc./sec. If a linear relationship can be assumed between the concentration of iron and the amount of Mn^{56} activity, the 0.01 ppm of iron normally present in water would account for only 0.2 dis./cc./sec. of Mn^{56} . This represents only about 2 percent of the amount of Mn^{56} normally present in the discharge water.

The relative insignificance of iron as compared to manganese in the production of Mn^{56} can be further illustrated by comparing Figure I with Figure IV. During the iron addition, the counting rate of 150 cc samples reached a value only about twice normal, even after 8 hours addition. At least 85% of this increase is estimated to be due to copper. As a result of the addition of 0.117 ppm manganese, the counting rate on these samples reached a level 8 times normal after 4-1/2 hrs; this large increase being due entirely to Mn^{56} .

The estimate of 2 percent as the maximum contribution of iron to the Mn^{56} activity in pile discharge water must be considered only as a maximum figure and not as a quantitative measurement of the cross section of the $\text{Fe}^{56}(\text{n},\text{p})$ reaction. The unidentified activity which was ascribed to Mn^{56} for the purpose of estimating a maximum is, in all probability, a mixture of components. The actual amount of Mn^{56} in this mixture could not be determined.

Support for the conclusion that an insignificant amount of Mn^{56} activity is produced from iron was found in an earlier test in which the activity induced in horizontal rod cooling water containing a varying amount of iron was measured (Interim Report on Production Test 105-2-P, "Activity of Pile Discharge Water", Document No. 3-3222, September 26, 1945). In this test, the Mn^{56} activity increased with iron concentration, but the increase was too slight to be significant unless increased many fold due to sticking of iron in the tubes. Considerable uncertainty surrounded the determinations of the iron content of the rod cooling water since iron rust sometimes enters the samples from the sampling line. The relatively greater number of fast neutrons in shim rod water was not accompanied by an increased ratio of Mn^{56} to other activity components in the shim rod water. These factors led to the conclusion that the increase in Mn^{56} activity with iron concentration was probably due to manganese impurity in the iron rather than to any reaction on the iron itself. All results obtained to date are consistent in this regard.

A steady increase in pressure drop occurred in Tube No. 2465 throughout the time iron was being added. The initial and final values of pressure drop were 7 p.s.i. and 51 p.s.i. respectively. An increase of about 2°C in outlet temperature also resulted from the film deposition. The contents of the tube

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were discharged and replaced with new metal, April 2, after which the pressure drop was about 10 p.s.i. The film deposit was undoubtedly ferric hydroxide, which formed when the feeder solution, having a pH of 2, entered the main cooling stream, where the pH was about 7.6. Visible amounts of gelatinous hydroxide precipitate settled to the bottoms of sample bottles which were allowed to sit for several days.

The manner in which a large amount of Mn^{56} activity results from a small amount of manganese impurity in the water has now been demonstrated. The source of this manganese impurity is almost certainly the Ferrifloc (ferric sulphate) which is used as a coagulant in the filter plant. This substance was shown to be the only additive used in water treatment which contains an appreciable amount of manganese impurity (Final Report on Production Test 305-6-P, "Activation of Process Water Additives", Document No. 3-3398, January 29, 1946). The factors which are responsible for consistently high Mn^{56} activity in one area while other areas are normal, remain to be determined. The purity of Ferrifloc is known to vary widely but it is extremely unlikely that one area would receive all of those shipments of Ferrifloc containing more impurity. It is known that high Mn^{56} activity usually occurs during periods when the iron concentration in the water is higher and larger amounts of sodium silicate are used for control of film formation. The same factors which permit more iron to escape removal in filtration possibly permit more manganese to remain in the water. Manganese precipitates as the hydroxide at a pH in the neighborhood of 8. Small variations in the pH at the filter plant as a result of differences in amounts of Ferrifloc and lime, may have a pronounced effect on the solubility of the manganese. The subsequent addition of variable amounts of sodium silicate also changes the pH of the water. The amount of manganese dissolving in the water probably depends upon the amount of ferrifloc, its purity, and the pH at which filtration occurs. The final amount of Mn^{56} activity is probably a function of the amount of manganese in the water and the pH of the water as it enters the operating unit. The decreased tendency of active manganese to settle out on surfaces in a water stream, at lower values of pH has been shown (Interim Report on Production Test 105-2-P, "Activity of Pile Discharge Water", Document No. 3-3222, September 26, 1945).

In normal operation, variables in the water treatment are seldom changed singly. For example, an increase in Ferrifloc feed is accompanied by the addition of a greater amount of lime in order to maintain a constant pH. As a result of systematic multiple changes such as this, efforts to correlate water activity with changes in water treatment have been largely fruitless. (Correlation Analysis of Water in 107-B, Document No. 3-2286, May 1, 1945 and Correlation Analysis of Water in 107-F, Document No. 3-2861, June 23, 1945). Special experiments in which individual additives are changed while other factors remain constant will be required to determine the exact mechanism responsible for the variability of the Mn^{56} component and bring about its correction.

W. B. JORDAN, CHIEF SUPERVISOR
100 - 300 TECHNICAL

J. M. West
J. M. West
100 Technical

JMW:jd

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FIGURE II
ACTIVATION OF MANGANESE
DISINTEGRATION RATES

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FIGURE III
DECREASE OF Mn^{56} ACTIVITY WITH TIME
(manganese addition stopped 3:42 p.m.)

COUNTS PER MINUTE ABOVE NORMAL

6 HOUR HALF LIFE

20 MINUTE HALF LIFE

TIME

3:42 4 5 6 7 8 9 10 11 12

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IRON FEED (1.17 p.p.m.)

FIGURE IV
ACTIVATION OF IRON
Counting rates on 150 c.c. samples

CODE
● No iron being added
X 1.17 p.p.m. iron added

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