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DEPARTMENT OF MINES AND TECHNICAL SURVEYS

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MINES BRANCH INVESTIGATION REPORT IR 63-70

PRELIMINARY STUDIES ON THE CONTAMINATION OF STEAM CONDENSATE AT DND (ARMY) CENTRAL HEATING PLANTS, FORT CHURCHILL, MANITOBA

by

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MINERAL PROCESSING DIVISION

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SUMMARY OF RESULTS

Contamination of the condensate is caused by high concentrations of ammonia, carbon dioxide, and volatile organic matter which seem to accumulate in stagnant areas of the system, such as closed radiators. The ammonia corrodes brass and copper parts of the system; the carbon dioxide corrodes iron parts as well as brass and copper; and the organic matter causes pungent odours.

These contaminants can be prevented from concentrating by regularly flushing all stagnant areas.

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INTRODUCTION

Morpholine treatment was not used to protect the condensate return line distribution system at these plants until early in 1962. Plant personnel suspected that this treatment was corroding brass and its use was discontinued for a time. On further direction by this Section, morpholine is again being used because there is no evidence that it is corrosive to brass and copper in condensate systems.

In the Monthly Boiler Water Treatment Control Service Report of July 13, 1962 the writer reported a deposit from a brass fitting, located at a convertor in building PMQ-20, to be basic copper carbonate and lead carbonate. It was concluded that carbonic acid in the condensate was the corroding agent. Subsequently, some condensate samples showed very high ammonia contents and during storage developed a very pungent odour. A high ammonia content was also found in a sample from a radiator in a Department of Public Works plant in Ottawa and in another DND plant. These samples also developed pungent odours during storage.

The writer visited the plants at Fort Churchill, September 24 to 27, 1962, to investigate the cause of the condensate contamination. At that time plant personnel reported that when it was necessary to repair certain parts of the condensate system, a very disagreeable odour was occasionally noted upon opening the system. The odour was particularly strong at radiators, even when the condensate was not being treated.

PROCEDURE

Condensate samples and the radiator value deposit were analysed according to procedures currently used in the Mineral Processing Division's laboratories. In addition to chemical analyses, ultraviolet absorption values were measured on condensate samples with a Beckman DU spectrophotometer over the range 200 to 300 mu.

An inspection of steam and condensate distribution systems was made to determine if the condensate was being contaminated by some outside source.

RESULTS

Table 1 shows the X-ray analysis of the green deposit taken from a brass radiator valve, and Table 2 reports the analyses of condensate samples.

TABLE 1

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X-ray Analysis of Green Deposit from Radiator Valve

| Location | Constituent found |
|-------------------------------|--|
| Main plant, building J-151 | Basic copper carbonate (CuCO ₃ .Cu(OH) ₂) |

* Analysis done by R.M. Buchanan, Head, Ore Mineralogy Section, Mineral Processing Division.

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Analyses of Condensate Samples

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|--|--------------------------|--------------------------|--|---|------------------------------|------------------------------|--------------------------|--------------------------------|--------------------------|
| le tion | pH | | | orenge orenge do _o) | ad 1ron n Fe) | ad copper a Cu) | د، | Ultra- violet absorption | |
| Sample location | Laboratory | 0n-the-site | Phenolphthal alkalinity (ppm CaCO ₃) | Methyl Orar alkalinity (ppm CaCO ₃) | Dissolved mqq) | Dissolved (ppm (| Armonia (ppm NH3) | 230 mu | 290 mu |
| Condensate tank, E10 Line under DOT quarters,A32 Radiator in dining room, C7 First radiator in hall to dentist's office, C4, | 7•7 7•0 7•2 | 8.5 6.2 7.1 | 0 0 0 | 28 21: 21: 21: | 0.00 0.00 0.00 | 0.05 0.37 0.09 | 0.1 0.5 0.1 | 0.040 0.335 0.044P | 0.023 0.104 0.022P |
| before flushing First radiator in hall to dentist's office, C4, | 7.6 | 6.2 | 0 | 68 | 0.00 | 0.47 | 12,5 | 0.242P | 0.100P |
| after flushing Condensate tank, J208 Line in convertor room, F26 Line in convertor room, F20 Line after radiator turned | 7.6 7.6 7.8 7.7 | 7.2 7.7 8.1 7.6 | 0 0 0 0 | 48 32 32 34 | 0.00 0.00 0.00 0.00 | 0.30 0.02 0.04 0.04 | 3.0 0.2 0.2 0.2 | 0.140P 0.030 0.035 | 0.064P 0.014 0.016 |
| on, J 128 Tank in convertor room, F21 Condensate tank, J 30 | 7•4 7•9 7•6 | <6 7•9 8•5 | 0 0 0 | 36 36 32 | 0.00 0.00 0.00 | 0.11 0.03 0.07 | 6.0 0.1 0.2 | 0.304P 0.035 | 0.140P 0.014 |

P- denotes peak at the respective wave length

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DISCUSSION

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Table 1 shows that the green deposit from the radiator valve is mainly basic copper carbonate, which is probably formed in the following manner. When the radiator is closed, condensate, containing appreciable dissolved carbon dioxide (carbonic acid), attacks the copper of the brass valve. At the same time the contaminant, ammonia as ammonium hydroxide, causes precipitation in-situ of this copper as copper hydroxide. Apparently, the concentration of ammonium hydroxide is insufficient to form the soluble copper ammonium complex. Opening of the radiator valve exposes the copper hydroxide to additional condensate, containing carbonic acid, and results in the formation of the green basic copper carbonate and probably further attack on the brass. This cycle is repeated every time the radiator is opened and closed.

The pH of the condensate (Table 2) varies considerably. The sample collected at the first radiator in the dentist's office had a field pH of 6.2 and a laboratory pH of 7.6; the ammonia in this sample was 12.5 ppm and the alkalinity as $GaCO_2$, 68 ppm. These results indicate that a considerable excess of carbon dioxide was present when the sample was tested in the field and that the rise in pH was due to the loss of carbon dioxide during shipment and storage. Also, the low pH, high ammonia, and high alkalinity values indicate that the ammonia is not present as free ammonia but is combined with carbon dioxide as ammonium bicarbonate. The copper content of this sample is a further indication of carbonic acid attack on brass and/or copper.

No technical literature has been found which shows that morpholine breaks down to form ammonia. Jacklin reports no significant breakdown at operating pressures and temperatures considerably higher than those at these plants (1). Also, investigations carried out at two other DND(Army) central heating plants did not show any appreciable quantity of ammonia in the condensate (2) (3).

According to Werner, carbon dioxide tends to accumulate in the vapour and gaseous phase in voided spaces at concentrations of several hundred to more than a thousand parts per million before equilibrium is reached. Cooling and low flow in lines allows considerable carbon dioxide to go into solution. The condensate pH is therefore lowered and corrosion becomes more serious on horizontal lines and at fittings and equipment where small quantities of condensate are retained (4).

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The ultraviolet absorption values (Table 2) are an indication of organic matter and/or of undetermined interferences. Ammonium hydroxide and ammonium carbonate did not show the same absorption values in the ultra violet range of the spectrum. It is reported that organic matter can cause very pungent odours in distribution systems (5).

Free and combined carbon dioxide, ammonia, and volatile organic matter in the make-up water, as well as the small amount of volatile organic matter in some of the organic conditioning agents volatilize with the steam, enter the distribution system, and concentrate in stagnant areas. Decay of the volatile organic matter could result in disagreeable odours in the condensate from these areas.

RECOMMENDATIONS

- 1. Morpholine treatment must not be stopped unless by authorized personnel because it is necessary to prevent corrosion of the steam and condensate distribution systems by aggressive carbonic acid.
- 2. To prevent the accumulation of high concentrations of ammonia and carbonic acid, and to eliminate the pungent odours caused by organic matter all stagnant areas of the system, should be regularly flushed.
- 3. To reduce the amount of undesirable volatile organic matter entering the system every effort should be made to recover as much condensate as possible and, thereby, reduce the amount of make-up water.

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