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RESEARCH MEMORANDUM

EFFECTIVENESS OF INHIBITORS FOR MASS TRANSFER AND CORROSION IN SODIUM HYDROXIDE - NICKEL SYSTEMS

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NATIONAL ADVISORY COMMITTEE
FOR AERONAUTICS

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EFFECTIVENESS OF INHIBITORS FOR MASS TRANSFER AND CORROSION IN SODIUM HYDROXIDE - NICKEL SYSTEMS

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SUMMARY

Static crucible tests with additions of the reducing agents sodium chromite Na_3CrO_4 and manganese dioxide MnO_2 indicate that salts soluble in sodium hydroxide may be added to inhibit mass transfer in nickel. The metals manganese, vanadium, and molybdenum were also investigated in static crucibles and found to be ineffective.

Toroid corrosion tests showed that complete exclusion of air is necessary to obtain maximum inhibition with chromium addition.

INTRODUCTION

Studies (ref. 1) at the Lewis laboratory have indicated that chromium additions to sodium hydroxide are effective in decreasing mass transfer in nickel crucibles and toroids. This inhibiting property is believed to be due to an intermediate of the type sodium chromite Na_3CrO_3 (ref. 2), which is formed. As a result of these studies, it was of interest to investigate, in static crucibles, the possible usefulness of other metals that could react with the caustic to form salts having similar reducing properties. The metals investigated were manganese, vanadium, and molybdenum. The possibility of adding salts directly was also studied using sodium chromite Na_3CrO_3, manganese dioxide MnO_2, and sodium nitrite $NaNO_2$.

Toroid results have been reported previously (ref. 1) for additions of 1 percent of chromium. In the experiments of reference 1 the standard method of sealing a toroid was modified to provide for complete exclusion of air by sealing the toroid in a helium atmosphere. A second purpose of this investigation was to learn whether the usual method of sealing in the open was sufficient to produce the observed beneficial effect. Accordingly, tests were run under both conditions without the additive and under the standard sealing method with 1 percent chromium.

EXPERIMENTAL PROCEDURES

Static Test

The static crucible experiments were carried out according to the procedures described in reference 3. The nickel crucibles (fig. 1) were mounted in a furnace that provided a hot-zone temperature of 1500° F at the bottom of the crucible and a temperature drop of 45° F from the bottom to the liquid level. The additives were introduced as powders together with the sodium hydroxide (13.0±0.1 g) before the moisture and air were removed by evacuation and heating. The extent of corrosion and mass transfer was determined by the weight changes of disk specimens in the hot zone.

Toroid test. - The toroid circulating apparatus (fig. 2) and experimental procedure are described in references 4 and 5. Tests were made using nickel toroids at 1500° F with a temperature difference of 40° F. The flow velocity in all the experiments was 15 feet per second.

The standard method of sealing a toroid involved the following procedure: After evacuation to remove moisture and air from the sodium hydroxide had been completed, an atmosphere of helium was introduced into the toroid. The connecting tube was then removed in the air and a close fitting nickel plug was quickly inserted into the vent tube. Complete closure was finally accomplished by heliarc welding. To compare the standard method of closure with a modified method that provided for complete exclusion of air, the introduction of the nickel plug into the vent tube was performed in an atmosphere of helium instead of air.

The measurement of mass transfer was made at intervals during the experiments by means of X-ray shadowgraphs of the cooled section (fig. 3). The inside diameter of a 3-inch arc from the cooled portion of the toroid was measured at 25 positions on each shadowgraph. From these measurements the average internal cross-sectional area was calculated and its percentage decrease was used as a measure of mass transfer during the experiment.

RESULTS AND DISCUSSION

Static Tests

The experimental results obtained in static crucible tests are shown in table I. Additions of Mn, Va, Mo, and $NaNO_2$ all resulted in higher mass-transfer rates than that observed with the NaOH alone. However, a decrease in rate similar to that found with Cr (ref. 1) was obtained with both Na_3CrO_3 and MnO_2. In both of these cases the specimens showed little evidence of attack and were coated with a thin layer of nonmetallic deposit. This behavior was identical with that observed for chromium additions (ref. 1). From these results it can be concluded that both Na_3CrO_3 and MnO_2 are effective in reducing mass transfer. However, further experimentation is necessary to determine the optimum concentrations and the behavior of these additive under forced-circulation conditions.

Toroid Tests

The results of the circulating loop experiments are presented in figure 4. The method of closure had little effect on the tests with pure caustic; the variations shown in figure 4 are believed to be of the order of magnitude of the errors inherent in the measurement of the reduction in area. The results with chromium addition indicate that the method of closure gives rise to greater difference. A test with 1 percent chromium in which the sealing was performed in air still yielded a much lower mass-transfer rate than either test with pure caustic at the same temperature difference. However, the rate was appreciably higher than that obtained when air was completely excluded (ref. 1). The inference is that the oxygen introduced from the air interferred with the reaction by which the chromium is effective, possibly by forming more than the usual amount of chromate (ref. 2), which is known to be detrimental (ref. 3).

SUMMARY OF RESULTS

From this investigation of corrosion and mass transfer of sodium hydroxide - nickel system, it was found that:

1. Addition of the reducing agents Na_3CrO_3 and MnO_2 in static crucible tests indicates that salts soluble in sodium hydroxide may be added to inhibit mass transfer in nickel. Further evaluation of these additives is needed, especially under forced-circulation conditions.

2. The metals manganese, vanadium, and molybdenum and sodium nitrite investigated in static crucibles were ineffective in inhibiting mass transfer.

3. Toroid tests employing two methods of sealing the system showed that complete exclusion of air is necessary to obtain maximum inhibition with chromium addition.

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Lewis Flight Propulsion Laboratory
National Advisory Committee for Aeronautics
Cleveland, Ohio, December 12, 1955

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TABLE I. - RESULTS OF STATIC CRUCIBLE TESTS

[Nickel crucibles at 1500° F with a temperature difference of 45° F and a test duration of 24 hr.]

Additive	Specimen weight change, mg
None	-5.0
Na_3CrO_3,[a] 1 percent	-2.9
Na_3CrO_3,[a] 3 percent	3.4
Na_3CrO_3,[a] 5 percent	6.3
MnO_2,[b] 1 percent	-4.2
MnO_2,[b] 5 percent	-2.9
Mn, 1 percent	-14.1
Mn, 3 percent	-35.0
Mn, 5 percent	-41.9
Va,[c] 3 percent	-49.4
Va,[c] 5 percent	-82.2
Mo, 1 percent	-20.1
Mo, 3 percent	-71.2
Mo, 5 percent	-165.3
$NaNO_2$, 1 percent	-15.1
$NaNO_2$, 3 percent	-35.6

[a]17.9 Percent Cr by analysis.

[b]C.P. 85 Percent MnO_2.

[c]Evolved H_2 upon purging.

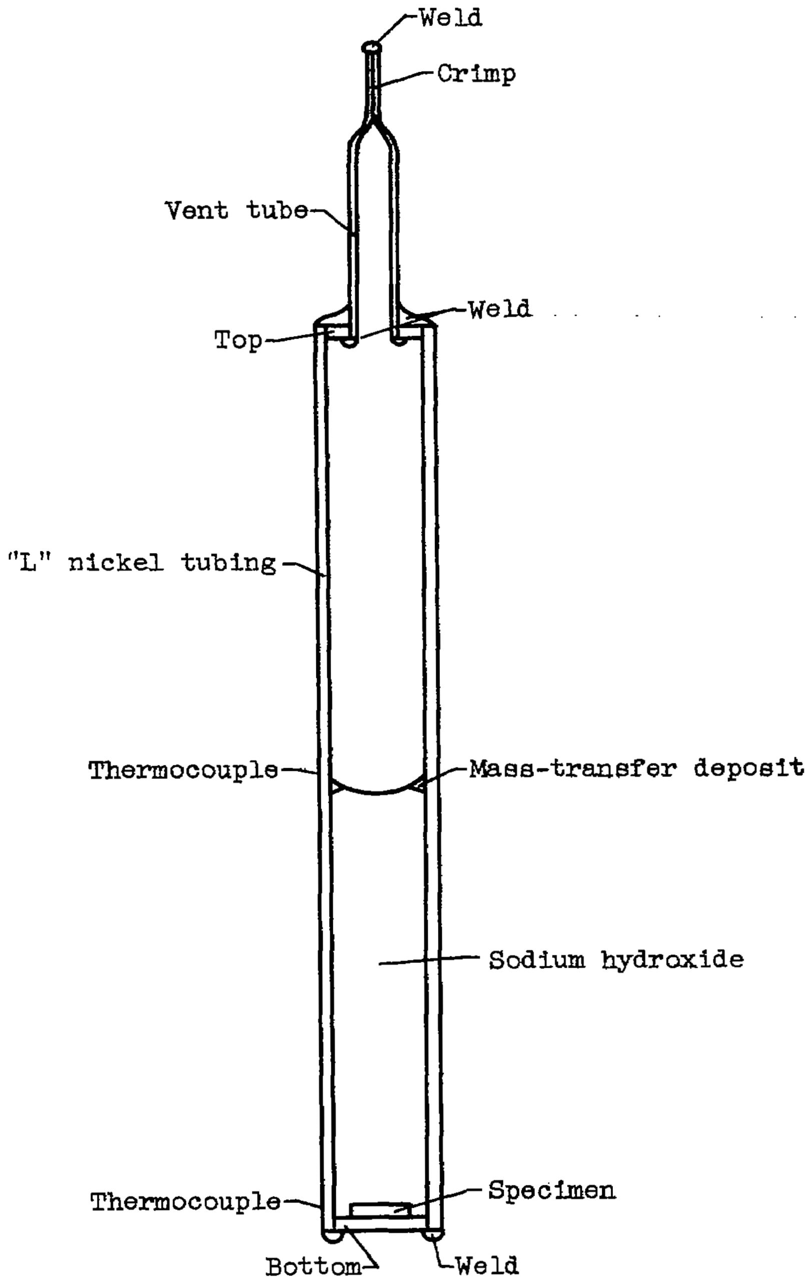

Figure 1. - Static crucible.

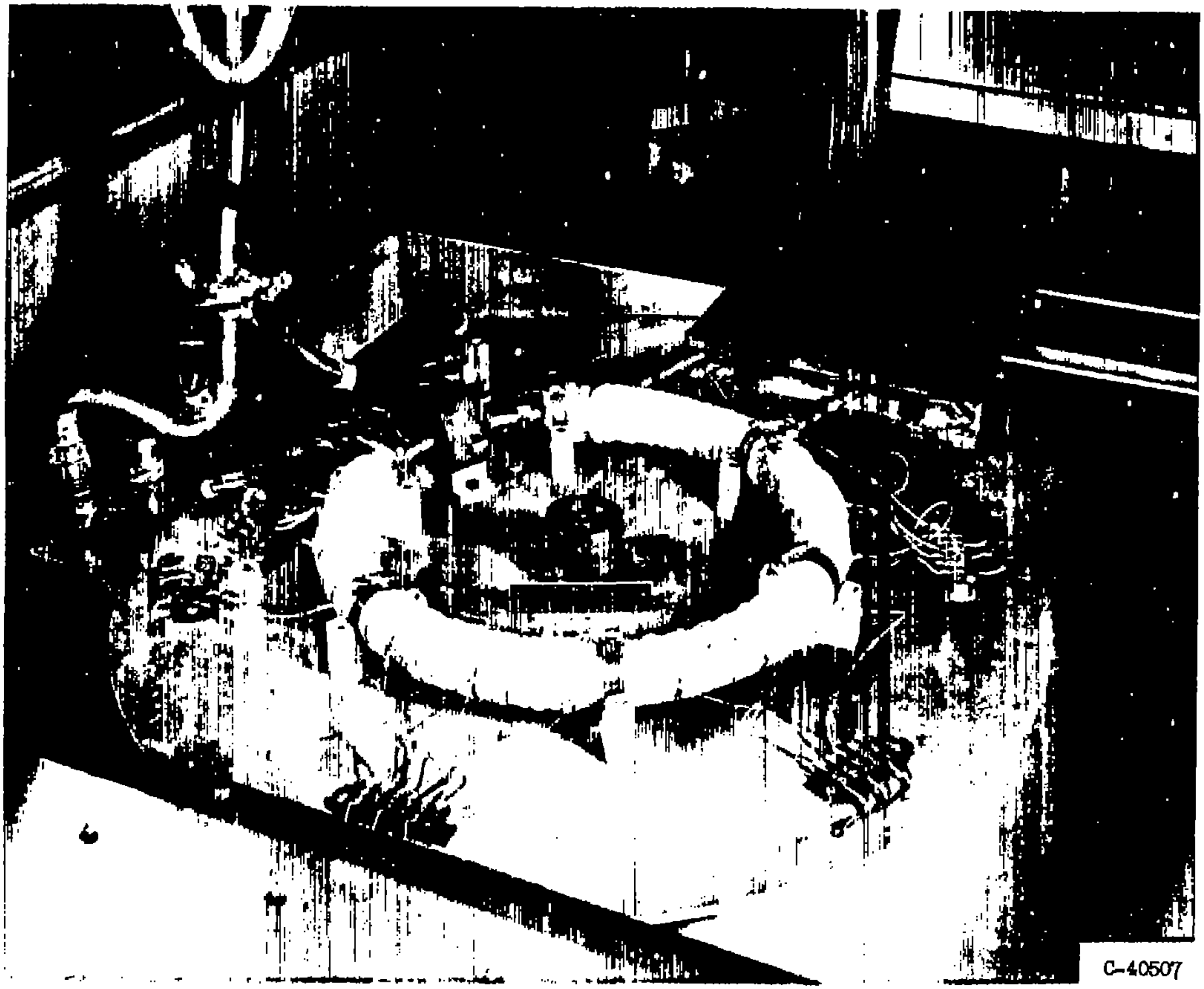

Figure 2. - Instrumented toroid and circulating apparatus.

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Figure 3. - Representative shadowgraph showing mass-transfer deposit in cooled section of toroid.

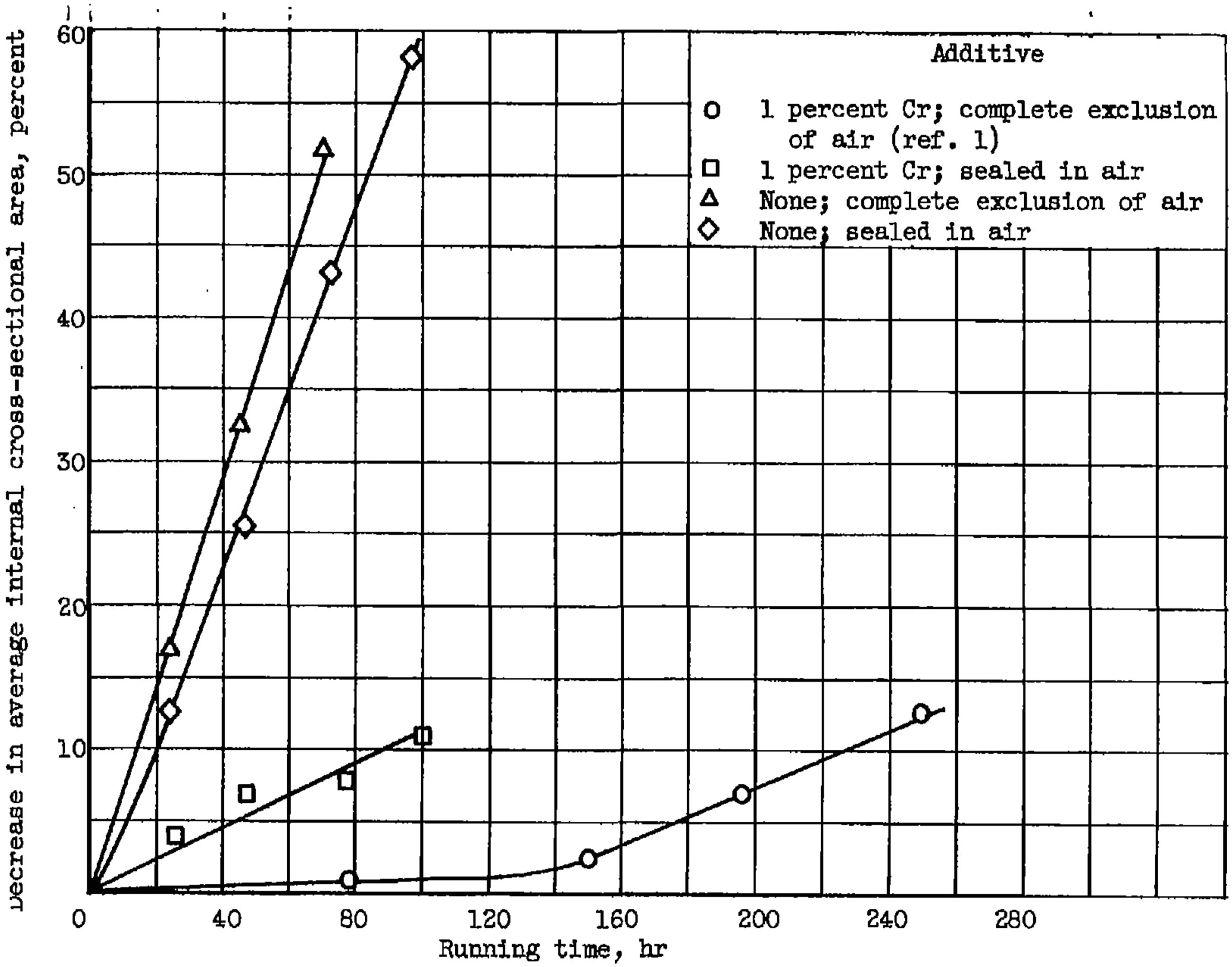

Figure 4. - Decrease in average internal cross-sectional area of cooled section with running time for nickel toroids operated at 1500° F with a temperature difference of 40° F and a flow velocity of 15 feet per second.