SIMPLE EXPERIMENTS STUDYING THE CATASTROPHIC CORROSION
OF STAINLESS STEEL CAUSED BY SODIUM LEAKS

by

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SUMMARY

Under certain conditions, small quantities of sodium escaping through a small hole may cause extensive corrosion and cratering on the outside of the containment in the vicinity of the leak and there is a possibility that this might lead to a major rupture of the containment.

It is difficult to estimate such a corrosion rate by conducting post mortems after an incident because of the lack of precise information about times and temperatures.

Simple sodium burning experiments have therefore been carried out in an attempt to provide rough quantitative data on the size of these corrosion rates. These showed that the average rate of corrosion of specimens of 18.8.1 stainless steel beneath a burning pool of sodium was of the order of 0.05 cm/hr at 600°C and 0.005 cm/hr at 400°C.

Enhanced corrosion occurs at the periphery of the burning sodium. The rate of penetration will depend on the shape of the corrosion profile which exists in the affected surface. The times needed to penetrate different wall thicknesses of stainless steel pipework have been calculated for various corrosion profiles similar to those which have been observed after incidents in KEML.
INTRODUCTION

1. In the past it has usually been accepted as a safety principle by REML that so long as sodium rigs were designed in such a way as to prevent major leaks of liquid metal, the occurrence of very small leaks could be tolerated because it would be possible to detect them before any serious damage to the equipment could ensue. Recent experience suggests that this simple correlation of potential hazard with leak size may be seriously in error, and there is a growing awareness of the possibility that a small leak may have serious consequences.

2. It has become apparent that under suitable conditions the sodium escaping through a small hole may cause extensive corrosion and cratering on the outside of the containment and there is a possibility that this might lead to a significant rupture of the containment. By this process a small leak could ultimately be transformed into a major release of sodium.

3. Some examples of this type of failure have been reported already. For instance, Wagner and Starnes (1965) describe how a leak in a 304 stainless steel expansion tank at Hallum reduced a wall thickness from 0.31 to 0.035 in. before it was discovered, while Stroughan (1963) describes how a sodium leakage at 600-700°C on the twin-zone loop at Dounreay caused severe corrosion to some adjacent 18.8 stainless steel pipes. Failures of this type have also been experienced in KfK and have been described by Eickhoff (1966). In one of these (Fig. 1) the wall of a test section was eroded to a depth of 0.064 in thereby reducing its effective thickness by nearly a factor of 2. On another occasion mild steel supports standing in a tray of burning NaK were grossly attacked at the NaK/Air interface. This type of behaviour should be contrasted with the normal corrosion process which occurs at the rate of $\sim 10^{-5}$ in/yr.

4. The likelihood of such a sequence of events occurring in a sodium rig or reactor must influence the design philosophy of the containment and the detection and inspection procedures which are used. In order to assess the hazard in a particular system it is important to know the rate at which the 'catastrophic' corrosion occurs on the outside of the containment.

5. It is usually difficult to extract this information from a post-mortem on actual incidents on rigs. A typical sequence of events is as follows:

   i) Someone notices that an escape of sodium has occurred either by the appearance of the metal, oxidised fume or a fire and gives the alarm.

   ii) An investigation is conducted by a competent person which may take 10-15 minutes as a result of which a decision is taken to dump the rig.

   iii) Sodium is allowed to drain from the rig into a dump tank - a process requiring anything from minutes up to half an hour for completion. At some stage during this process, the level of sodium inside the rig will fall below the leak, after which no more sodium can escape.

   iv) Meanwhile, the sodium which has escaped may fire. Whether or not this occurs depends on the initial temperature of the system, the thickness of the lagging and the availability of oxygen or moisture, and the quantity of sodium which has escaped. The fire will burn for an indeterminate time, and the temperature reached will not be known unless a thermocouple happens to be situated in the vicinity.
Eventually when all the escaped sodium has oxidised or the supply of air exhausted (perhaps by the scaling effects of the solid oxidation products), the temperature will begin to fall at a rate determined by the thermal properties of the system.

When cold the damaged lagging will be removed and the metal surfaces examined.

It is clear that in most cases reliable data on times and temperatures are not available nor are the conditions needed to promote catastrophic oxidation properly understood, and the conclusions to be drawn from a study of incidents on sodium rigs are therefore usually only qualitative.

The present memorandum describes some simple experiments which were carried out in an attempt to augment the data on sodium fires by burning quantities of sodium in stainless steel boats at 400°C and 600°C and measuring the weight losses which resulted. In this way it was hoped to get rough values for corrosion rates under conditions resembling those which occur in catastrophic corrosion.

EXPERIMENTAL PROCEDURE

Burning Tests With Stainless Steel Boats at 600°C

Corrosion tests were carried out in small stainless steel boats. These were made by cutting standard sections of $\frac{1}{2}$ in and 1 in nb stainless steel pipe lengthways and forming the sections into 'boats' in a vice (Fig. 2). After cleaning and weighing, the boats were placed on a hot plate formed from a 12 in d. circular plate of mild steel $\frac{1}{2}$ in thick which was heated from below by gas torches. Heat was conserved by surrounding the assembly by a simple shield as shown in Fig. 3. The temperature was measured by a stainless steel sheathed thermocouple and when this had reached equilibrium, the burning experiment was started.

Pellets of sodium weighing about 1-2 grams were placed into the boats using long handled tongs and allowed to burn freely in the air. Measurements with the thermocouple probe showed the boat quickly regained a temperature of 600°C after addition of a sodium pellet. Burning times were extended by adding further pellets when the previous one ceased to burn. All the experiments were conducted outside the laboratory, on a burning ground some distance from the main building and personnel were suitably dressed in fireproof clothing. When the sodium had burnt for the requisite period, the boats were plunged into soda ash (anhydrous sodium carbonate powder), rinsed in water, dried and re-weighed. The average corrosion rate was deduced directly from the burning time and the weight loss of the boat.

In order to see whether the corrosion rate was influenced by a presence of lagging a variation in procedure was adopted. Loose pieces of the appropriate kind of lagging were piled into the boats and allowed to reach equilibrium temperature. Pellets of sodium were then placed on top of the lagging. During the subsequent fire, molten metal trickled down through the loosely heaped lagging ensuring intimate contact with both lagging and the stainless steel boat.

Additional tests were also carried out to compare the corrosive effects of burning sodium metal with those of the molten caustic residues which are the end product of a sodium fire. This was done by collecting together the molten residues which remained after combustion was complete and pouring them into a clean weighed boat held at the appropriate temperature. In this way it was hoped to get rough values for corrosion rates under conditions resembling those which occur in catastrophic corrosion.

2.
Burning Tests with Stainless Steel Boats at 400°C

12. Following on from the corrosion tests at 600°C, a further series of tests was carried out at 400°C. The specimens used were again made from 1 in NB 18.8.1 SS pipe, but were made longer than before, the nominal weights being 100 grams.

13. The same techniques were employed as before, the burning metal being replenished by extra pallets of sodium. In general, the sodium was slow to fire, and induction periods as long as 15 minutes were noticed. As burning progressed the specimen became covered with a thick solid layer of oxidation products which gradually spread over the whole area and contaminated the lower sides of the boats. For this reason the burning was not very uniform and it was allowed to continue for periods up to 30 minutes.

Tests with a Lagged Pipe Section

14. A typical rig section was also subjected to a burning sodium test. The model consisted of a 9 in length of 2 in NB stainless steel pipe, fitted with tape heating and stillite lagging. For the purpose of the test a portion of the lagging was scooped out and filled with about 300 grams of solid sodium.

15. The section was placed on the hot-plate in a horizontal position and heated to about 500°C and the sodium allowed to burn to completion, which took about half an hour. After cooling the pipe was cleaned and inspected.

RESULTS AND DISCUSSION

16. The results of the first series of tests using small (30 g) boats at 600°C are listed in Table 1. The weight losses have been converted to penetration rates on the assumption that the corrosion was uniform and that the average area of the boat in contact with liquid sodium was 15 cm².

<table>
<thead>
<tr>
<th>Test No.</th>
<th>Type of Test</th>
<th>Loss in Weight (g)</th>
<th>Burning Time (min)</th>
<th>Average Penetration Rate cm/hr</th>
</tr>
</thead>
<tbody>
<tr>
<td>a 2</td>
<td>Pure Sodium</td>
<td>0.407</td>
<td>3</td>
<td>0.082</td>
</tr>
<tr>
<td>a 3</td>
<td></td>
<td>0.729</td>
<td>4</td>
<td>0.092</td>
</tr>
<tr>
<td>a 4</td>
<td></td>
<td>1.05</td>
<td>6</td>
<td>0.089</td>
</tr>
<tr>
<td>a 5</td>
<td>Sodium and Stillite</td>
<td>1.48</td>
<td>8½</td>
<td>0.098</td>
</tr>
<tr>
<td>a 6</td>
<td></td>
<td>1.54</td>
<td>10½</td>
<td>0.094</td>
</tr>
<tr>
<td>a 7</td>
<td>Sodium and Rocksill</td>
<td>1.38</td>
<td>8</td>
<td>0.087</td>
</tr>
<tr>
<td>a 9</td>
<td></td>
<td>1.53</td>
<td>10</td>
<td>0.077</td>
</tr>
<tr>
<td>a 10</td>
<td>Caustic Residues</td>
<td>0.05</td>
<td>30</td>
<td></td>
</tr>
</tbody>
</table>
The data given in Table I is also presented in Fig. 4 which shows the weight losses as a function of time of burning. A linear relationship is evident. These experiments showed that the corrosion rate stayed roughly constant and corresponded to a penetration rate of just less than 1 mm per hour. The presence of lagging seemed to have a negligible effect on the corrosion and the caustic residues were less corrosive than burning sodium.

In order to achieve greater control over the experimental conditions and in particular to define more accurately the area over which the corrosion took place, the experiment was repeated using larger boats (75 g).

As before, the overall amount of corrosion was measured by weighing the boats before and after the experiment with the results shown in Table II. The penetration rates were again calculated on the assumption of uniform corrosion. In these experiments the average area of contact between sodium and the stainless steel boat was 35 cm².

### TABLE II

Corrosion of 75 g boats by burning sodium at 600°C

<table>
<thead>
<tr>
<th>Test No.</th>
<th>Type of Test</th>
<th>Loss in Weight (gms)</th>
<th>Burning Time (Min)</th>
<th>Average Penetration Rate cm/hr.</th>
</tr>
</thead>
<tbody>
<tr>
<td>B 1</td>
<td>Fed with sodium, the excess caustic melt drained away every 10 minutes.</td>
<td>6.74</td>
<td>30</td>
<td>0.049</td>
</tr>
<tr>
<td>B 3</td>
<td>As above</td>
<td>12.18</td>
<td>60</td>
<td>0.044</td>
</tr>
<tr>
<td>B 4</td>
<td>No sodium, Pure caustic melt only.</td>
<td>1.17</td>
<td>60</td>
<td>0.004</td>
</tr>
<tr>
<td>B 2</td>
<td>Control specimen, No sodium, but slight contamination with caustic on the base.</td>
<td>0.18</td>
<td>60</td>
<td>0.0006</td>
</tr>
</tbody>
</table>

The sodium corrosion rates measured in Tests B1 and B3 were self consistent and differed from those obtained with the small boats by less than a factor of 2. As before, the caustic residues were much less potent a source of corrosion than the burning sodium.

Besides noting the net losses in the specimens, the change in thickness of the boat used in Test B3 was measured by means of a micrometer. The results confirmed the visual impression that the corrosion was greater in the peripheral region than beneath the bulk of the liquid sodium. A schematic diagram of the corrosion zones is shown in Fig. 5. The central region with an area of 18.5 cm² was permanently submerged in sodium for 1 hour and decreased in thickness by 0.030 cm during the course of the experiment. By contrast, the peripheral zone was corroded to an average depth of 0.054 cm. To account the areas of the two zones, the calculated weight loss corresponding to the decrease in thickness of the boat was within 10% of the directly measured value.
22. Enhanced corrosion rates in the peripheral region might well explain the rather higher penetration rates obtained with the smaller boats because edge effects would be expected to be greater in this case.

23. Even larger boats were used to measure the smaller corrosion rates obtained with sodium at 400°C. The results of the experiments are given in Table III.

**TABLE III**

Corrosion of 100 g boats by burning sodium at 400°C

<table>
<thead>
<tr>
<th>Test No.</th>
<th>Type of Test</th>
<th>Exposure Time (Min)</th>
<th>Weight loss (gm)</th>
<th>Penetration Rate cm/hr</th>
</tr>
</thead>
<tbody>
<tr>
<td>C 5</td>
<td>Molten Sodium</td>
<td>18</td>
<td>0.012</td>
<td>-</td>
</tr>
<tr>
<td>C 6</td>
<td>Molten Sodium Burning Sodium</td>
<td>18</td>
<td>30</td>
<td>1.54</td>
</tr>
<tr>
<td>C 7</td>
<td>Molten Sodium Burning Sodium</td>
<td>5</td>
<td>15</td>
<td>0.47</td>
</tr>
<tr>
<td>C 8</td>
<td>Molten Sodium Burning Sodium</td>
<td>4</td>
<td>30</td>
<td>0.93</td>
</tr>
<tr>
<td>C 9</td>
<td>Molten Sodium Burning Sodium</td>
<td>5</td>
<td>30</td>
<td>0.59</td>
</tr>
<tr>
<td>C 10</td>
<td>Molten Sodium Burning Sodium</td>
<td>4</td>
<td>30</td>
<td>0.48</td>
</tr>
</tbody>
</table>

24. Although some corrosion did occur in the lower side of the boat because of the higher concentration of the reaction products, the pessimistic assumption is made that all the attack was concentrated in the upper surface of the boat with an area of 60 cm^2. The results of Test C5 show that weight losses during the induction period before the sodium fire could be ignored and the penetration rate is therefore calculated on the assumption that all the measured weight loss occurred whilst the sodium was actually burning. The increased scatter in the results is hardly surprising in view of the difficulty of maintaining steady burning in the presence of large quantities of solid reaction products. In general the rates are down by more than an order of magnitude compared with those at 600°C.

25. From the point of view of rig safety, the vital piece of information from corrosion studies is the measured rate of penetration under the most adverse conditions which can be encountered and attention has already been drawn to the fact that during a sodium fire, peripheral corrosion occurs with considerable rapidity. A good example of this was the behaviour shown by the leached pipe specimen (para. 14). Its general appearance at the end of the experiment is shown in Fig. 6 in which the 'tide mark' surrounding the zone containing the liquid sodium can be seen quite clearly. In some places, notably on the underside of the pipe where the sodium/steel air interface was well defined, the tide mark consisted of the deep fissure shown in Fig. 7. By taking a cross section of the corroded area (Fig. 8) the depth of penetration was shown to be 0.013 cm. This corrosion occurred at a normal temperature of 500°C during a period of not more than half an hour. The rate of penetration under these conditions was therefore 2.025 cm/hr.
26. Enhanced corrosion rates were also clearly observed in Test No. B3 with the 75 gm boat in which the mean corrosion rate in the peripheral region was 0.06 cm/hr compared with 0.03 cm/hr beneath the sodium surface. It is likely that as the sodium burnt and was replenished the interface moved backwards and forwards across the peripheral zone. Had it remained stationary, it is reasonable to suppose that the penetration would have been appreciably greater.

27. How much greater would depend on the profile of the corroded region. Various examples of possible profiles are illustrated in Fig. 9. The most serious profile is No. 4, consisting of a pit deepening but without widening. Although the occurrence of such a fault is unlikely, its consequences have been included for purposes of comparison. The evidence from post mortem incidents in RML rigs suggests that if a profile of this type were to occur it is unlikely that its width would be less than 0.1 cm.

28. From the results of the first series of tests, Fig 4, it is concluded that the weight loss per unit time and hence the volume loss per unit time are constant. If the perimeter of the corroded area remains fixed, it follows that the rate of increase of the area of the corrosion profile remains constant.

29. In the case of the 3rd test on the 75 gm boat the average width of the peripheral zone was 0.8 cm and the average depth of penetration after 1 hour was 0.051 cm. Hence the area of the corrosion profile increased at the rate of \((0.8 \times 0.051) = 4.08 \times 10^{-2} \text{cm}^2/\text{hr}\). By combining this figure with the expressions for the areas of the various corrosion profiles in Fig. 9 it is possible to calculate the time needed for the maximum depth penetra (p) to equal any specified value. Table IV lists the times needed to penetrate various wall thicknesses of stainless steel piping.

TABLE IV

Calculated times needed to penetrate various wall thicknesses of 18.8.1 stainless steel pipework at 600°C

<table>
<thead>
<tr>
<th>Type of Pipe</th>
<th>Penetration Times for different corrosion profiles (hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Nominal Diameter (in)</td>
</tr>
<tr>
<td>24</td>
<td>0.25</td>
</tr>
<tr>
<td>14</td>
<td>0.189</td>
</tr>
<tr>
<td>4</td>
<td>0.12</td>
</tr>
<tr>
<td>2</td>
<td>0.109</td>
</tr>
</tbody>
</table>

30. It will be seen that the calculated penetration times vary widely depending on the geometry of the corrosion front. Moreover, if the local hot-spot temperatures near a leak in a piece of lagged pipe are significantly different from those occurring in the boats of burning sodium, the corresponding penetration times will be affected.
CONCLUSIONS

31. When sodium leaks from rigs at temperatures of 400°C or above it usually fires, resulting in extensive corrosion of the adjacent external surface of the containment. It is difficult to estimate corrosion rates by conducting post mortem on such incidents because of the lack of reliable information about times and temperatures.

32. Simple sodium burning experiments have been carried out in an attempt to provide rough quantitative data on the size of these corrosion rates. These showed that the average rate of corrosion of specimens of 18/8 stainless steel beneath a burning pool of sodium was of the order of 0.05 mm/hr at 600°C and 0.005 mm/hr at 400°C.

33. Enhanced corrosion occurs at the periphery of the burning sodium. The rate of penetration in this region will depend on the shape of the corrosion profile, which exists on the affected surface. The times needed to penetrate a stainless steel surface to a depth equal to the wall thickness of typical sizes of pipework have been calculated for various corrosion profiles, similar to those which have been observed in RNL incidents. These times vary considerably depending on the corrosion profile assumed. If the local hotspots temperatures are significantly different from those occurring in the boats of burning sodium, the corresponding penetration times will be affected.

REFERENCES

Eickhoff, Y J (1966) RTG Internal Document
Straughan, R (1969) D72 Internal Document
Wagner, R K and Stearns, J D (1965) CCFP 65030 p47
FIG. 1 CATASTROPHIC CORROSION AFTER A SODIUM LEAK ON THE F.E.T.T.R TEST SECTION IN R.E.L.
FIG. 2. STAINLESS STEEL BOATS USED IN BURNING EXPERIMENTS
FIG. 3  DIAGRAMMATIC SKETCH OF HOT PLATE
○ Boat containing burning sodium at 650°C
△ As above with added stillite
□ As above with added rocksill

**Figure 4.** Graph showing increasing wt loss with time.
FIG 5. APPEARANCE OF 75g BOAT AFTER TEST 3 (TABLE II)
SHOWING PERIPHERAL ATTACK BY BURNING SODIUM
FIG. 6 FINAL APPEARANCE OF LAGGED PIPE SPECIMEN
SHOWING TIDE MARK AROUND AREA IN CONTACT WITH

LIQUID SODIUM
FIG. 7. ENHANCED CORROSION AT THE EDGE OF THE SODIUM CONTAMINATED AREA IN FIG. 6.
FIG. 8. CROSS-SECTION OF FISSURE SHOWN IN FIG. 7.
1. **RECTANGULAR** (Axes in ratio of $2:5$)  
   
   ![Diagram of rectangular profile]
   
   AREA $= 2.5 \pi$

2. **TRIANGULAR** (Included angle of 120°)  
   
   ![Diagram of triangular profile]
   
   AREA $= \sqrt{3} \pi$

3. **SEMI-CIRCULAR**  
   
   ![Diagram of semi-circular profile]
   
   AREA $= \frac{\pi}{2} \pi$

4. **RECTANGULAR** (With small & constant width w)  
   
   ![Diagram of rectangular profile with constant width]
   
   AREA $= w \pi$

**FIG 9 EXAMPLES OF CORROSION PROFILES**
FIG 10  ENLARGEMENT OF FIG 1 a  SHOWING THE OCCURRENCE OF DIFFERENT TYPES OF CORROSION PROFILES