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English Translation

MODEL TEST OF Na POOL FIRES - No.2

December, 1969

SODIUM LABORATORY

JAPAN ATOMIC ENERGY RESEARCH INSTITUTE

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Abstract

Some preliminary informations on the burning condition of sodium and its influence to the container vessel in case of the sodium fire have been obtained from "Model Test of Na Pool Fires - No. 1".

The present experiments aim to have more detailed data for the same purpose.

The effects of the initial sodium temperature, the initial oxygen contents, and the natural convection in the vessel were clarified by the supplementary tests.

The apparatus for the previous tests was used also for the present tests being partially remodeled.

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§1 Test Purpose and Conditions

In respect to the design and the safety analysis of a fast breeder reactor, it is required to have a knowledge of the influence on a container vessel and burning condition of sodium when it burns in the vessel. Therefore "Model Test of Na Pool Fire - No.1" and its analysis have been carried out in the previous year, then it is planned to get more informations for safety evaluation from an additional test with the partially remodeled apparatus.

Since the vessel proper of $3.2m^3$, sodium combustion dish and sodium melting tank, each being used for the test, have been the same as they were in the previous test, the conditions of design and manufacturing are omitted.

Seven tests were made with the vessel proper, including a retest and also a comparative test was made in which a sodium combustion dish was placed open in air and a quantity of sodium was introduced into it to burn. Therefore total of eight tests were carried out.

Items and Conditions of the test are as follows:

1) A test for tracing purpose on the effect of humidity and initial oxygen concentration on sodium fire
   (30%RH, 15v/oO_2, 10v/oO_2) (RH stands for Relative Humidity)
2) To test on the effect of initial temperature of sodium upon the burning phenomena.
   (250°C, 500°C, 70%RH, 21v/oO_2, $0.15m^2$)
3) A test for tracing purpose concerning the ratio of the exposed surface area of sodium
   (S) to the sectional area of the vessel (So)
   (S/So = 0.0849, 0.0425)
4) A measurementof natural convection phenomenon in the vessel
   (Initial gas temperature at 100°C)
5) An observation of the sodium fire in the combustion dish of $0.075m^2$ large and 150mm deep which was placed open in air.

Measurement Items for the above mentioned are as follows:

1) Pressure variation in the vessel proper
2) Variation of oxygen concentration (during and after comburtion) in the vessel
3) Temperature variation at various places (in gas and the vessel proper)

4) Observation and recording of combustion condition for six cases (eight test runs) shown in Table 3.1

§2 Test Apparatus

2.1 Remodeling of The Test Apparatus

Account of Principal components of the apparatus are not given, because they have been the same as used in the commission study in 1968.

Models changed for the test are listed below:

1) Thermocouple fitted additionally to the vessel proper

Previously a dozen of sheath type thermocouple were inserted so as to measure gas temperatures in the vessel proper. In this test 32 pieces of thermocouple (1.6ø in sheath type) have been inserted providing with Conack seal of collective type in order to increase the number of measuring points and some of them were used for temperature measurements of liquid sodium on fire.

2) Replacement of Manometer

Because the manometer (a diaphragm type of pressure gauge with recorder) used previously had a wide range of indication of pressure from + 3kg/cm^2 to - 500 mmHg and were inferior in the precision of measurement, it was replaced with a remotely indicative pressure gauge of cell-meter type with contact point of ±1kg/cm^2, and the fitting flange was also remade.

3) A house of 2m x 4m flour area was extended in the south of the old building. The space was served to install and operate a gas chromatography, a pressure gauge, vidio corder and so forth, and very effective when it rained.

4) Supply of recorder thermometer

Two sets of recording type thermometer were provided. They are of 30 mV, changeable to CA.

Among repair works done were the heat insulation work, replacement of packing gland of valves, piping and heater, conduit pipe of sodium into the combustion dish.

2.2 Method of Test

The method of the test is not given because it has been carried out in the same manner as the previous report.

§3 Test Results

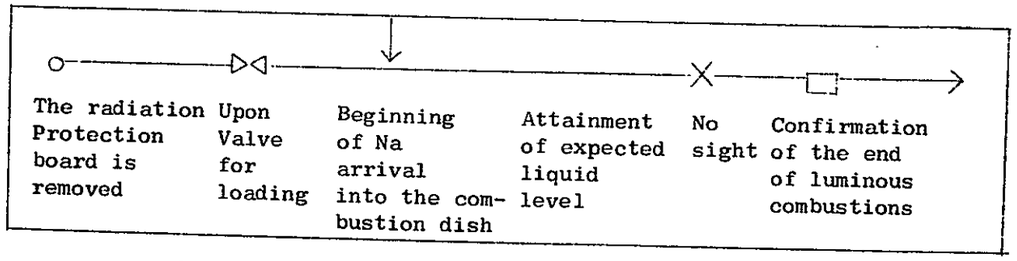
3.1 Test Process

Two kinds of combustion dish were used in six cases of the test (eight times in all). These test conditions and processes are shown in Table 3.1. Although there are two cases whose test conditions are quite the same, that is, the retest was carried out, since there have been differences to be noticed in combustion phenomena, because sodium of a different purity was used.

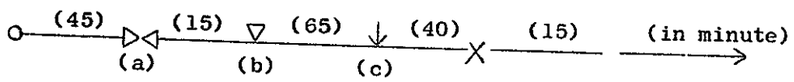
Sodium used for the test, except for Tests No.1 and No.2 in which the purity of sodium was as high as 99.97., was likely to be contaminated with such impurities as potassium and so on, because it had been recovered after the use for the loop operation. Analytical results of potassium are shown in Table 3.2. Sodium used for Test No.3 and thereafter was of technical grade and manufactured by Downs process (Manufacturer: Nihon Soda Mfg. Co.). Analytical result of this sodium is shown in Table 3.3. The sodium is of 99.85% of purity, but contains many impurities such as potassium, calcium and so on. Among others calcium is contained around 290ppm, that is 190ppm more than its saturated solubility at 100°C, and is seemed to be segregated to the bottom of a drum container. It is conceivable that sodium of high calcium content was obtained when it was introduced into the melting tank from this drum. Therefore there are influences to be observed in No.3 to 5 affected by the presence of calcium. Total amount of sodium directly used for the test was about 170 litre.

3.2 Combustion phenomena at each test (Time Sequence, etc.)

Legend



Test No.1 (Date) 6/2 (0.15m^2, 150m/m, 22.7ø, 500°C, 75%RH, 21v/oO$_2$)

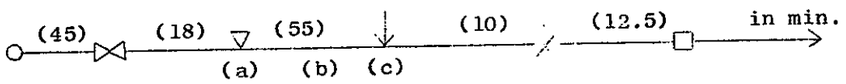


(a) A spark was observed immediately after the loading valve was opened.

(b) About ten firing spots were generated, expanding to the combustion.

(c) Firing spots were dispersed every where, resulting in the whole surface combustion. Although the level gauge of contact type was not worked normally, it is conceivable that sodium oxide generated on the liquid surface prevented it from the contact. The aspect of sodium fire after removing from the vessel proper is shown in Photo 3.1.

Test No.2 6/4(0.15m^2, 150m/m, 22.7ℓ, 250°C, 68%RH, 21v/oO_2)



(a) Firing spot was generated almost over the whole surface, and the combustion started on the spot and then spreaded.

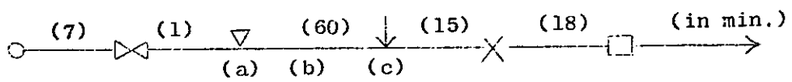
(b) Firing spot spreaded all over and the combustion was observed all over the surface.

(c) Flame was short but firing strong. The sight was reduced to the extent of 10% due to smoke.

The surface of sodium immediately after loading into the combustion dish was covered all over with metal oxide and did not show any metallic luster. The surface appearance of the combustion dish for sodium is shown in Photo.3.2. The liquid surface appears to be covered with combustion products.

Incidentally, fresh sodium (see Table 3.3) was loaded from the drum after the test had finished.

Test No.3 6/13 (0.15m^2, 150 m/m, 22.7ℓ, 250°C, 74RH, 21v/oO_2)



(a) As soon as sodium was loaded, a spark seemingly due to Ca was observed.

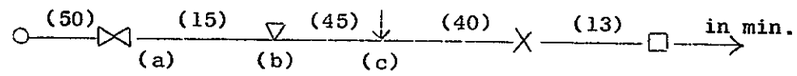
(b) Firing spots were generated at several places and the combustion started.

(c) Firing spots covered all over the surface and the combustion became more fiercely.

The appearance of sodium products on the surface of the combustion

dish in the vessel is shown Phote.3.3. It shows the aspect of the whole surface which was covered with combustion products.

Test No.4 6/16 (0.15m^2, 150m/m, 22.71, 500°C, 68%RH, 21v/oO_2)



(a) A flame of 30 40cm long was generated but subsided immediately.

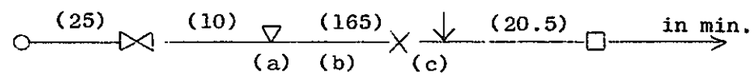
(b) Firing spots were generated and began to expand.

(c) Occationally a successive flame was observed

(d) The sight was expanded after 3 hours, the surface of sodium could be seen and appeared to have metallic luster.

The aspect of the combustion dish before washing deposited products is shown in Photo. 3.4.

Test No.5 6/18 (0.15m^2, 150 m/m, 22.7ℓ, 500°C, 70%RH, 15v/oO_2)



(a) Along with the fume, sodium was loaded

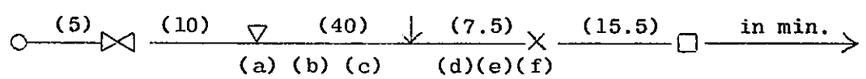
(b) Firing spots were observed at four to five places

(c) The sight became zero before liquid level expected has been attained.

(d) It is a bit unclear to identify the end point of luminous combustion.

In three hours after the combustion, it was confirmed that a thin layer of oxide covered over the surface of liquid sodium in the combustion dish. The combustion dish from which unreacted sodium was taken, is shown in Photo 3.5. After the end of the test sodium at 120°C was loaded again from the drum.

Test No.6 6/20 (0.075m^2, 150m/m, 11.3ℓ, 500°C, 35%RH, 11.2v/oO_2)



(a) Wrinkling in the layer of sodium oxide, the level of liquid went.

(b) Firing spots were observed at two places and they sustained for a while.

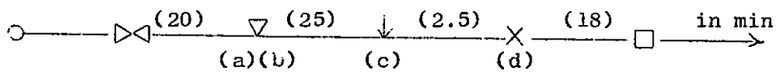
(c) Fuming was observed at the pointed surface, even if no firing spot had been seen.

(d) The temperature of the combustion dish was kept at 500°C.

(e) Rapid expansion of combustion could not be observed, but it proceeded rather slowly.

(f) At one place sodium creeped up, burning on the inner wall of the combustion dish.

Test No.7 6/24 (0.15m^2, 150m/m, 23ℓ, 500°C, 70%RH, 21v/oO_2)
Average gas temperature of 110°C)



(a) A spark was spotted at the same time when sodium was loaded.

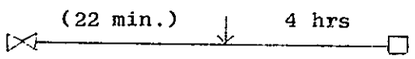
(b) Firing spots were observed at 3~5 places, a white layer of oxide was spreading out.

(c) Combustion started over a third of the surface area. Firing spots expanded some what slowly.

(d) Combustion over almost the whole surface.

The aspect of the combustion dish in four hours after fire was extinguished, is shown in Photo 3.6. The liquid surface of sodium appears to have a metallic luster.

Test No.8 7/23 (Out door Combustion Test 75%RH, 28°C, 0.075m^2, 180m/m, 13.5l, 500°C)



(a) Firing spots were generated at four to five places immediately after sodium was loaded, then they stretched out over the whole surface.

(b) A heave of combustion products was formed at only one place of the edge and inner wall of the combustion dish.

(c) Sodium dropped out of the hem 5.5 minutes later.

(d) A combustion on the surface of products heave ceased.

(e) After four hours, the combustion on the surface almost ceased.

Time sequence of combustion is illustrated by Photo (Photo.3.7.)

3.3 Summary of Observations on the Combustion Phenomena

3.3.1 The effect of Initial Temperature of the Combustion

(a) In case of the initial temperature at 500°C(No.1,4,7, with 21v/oO_2)

In all cases, firing spots were generated directly after sodium was loaded, and expanded to continue the combustion. As compared with the previous results, since the expansion rate of firing point was faster and it took only few minutes before it covered over the whole surface, moreover the aspects of development and a relatively short time such as 20 minutes were required for the cessation of fire, it is possible to anticipate that the combustion rate became faster than that in the previous report. The reason conceived for this phenomenon is that sodium used for the test was different from that of the previous year and contained much impurities,that is, in Tests No.1 and 2, the content of potassium and in Tests No.3 and thereafter the content of calcium, respectively were assumed to be present in greater amount. Those analytical results are shown in Tables 3.2 and 3.3. It is assumed that the segregation of in purities was present in the tank and piping, because of low temperature (about 120°C) for transportation.

The sight in the combustion vessel has broaden in two hours after the cessation of ignition combustion, and white smoke began to settle in the form of powder on the lower side of the vessel. This aspect is the same as that in the previous test, but the color of products, heaved on the upper edge of the combustion dish to the extent of 20~40 m/m and consisted of partially oxydized sodium evaporation deposit, is appeared to be blackish brown as if due to insufficient oxidation. Moreover, also the surface of un-reacted sodium left in the combustion vessel showed the same color (in case of Test No.1) or the tendency being covered with a thin layer of oxide film (in case of Test No.5). The appearance of a perfect mirror, however, as shown in the previous report was just obtained in case of Test No.7. Furthermore, at the bottom of liquid sodium with no reaction, a layer of precipitate of about 20mm thick was observed; this was thought to be made of sodium oxide due to the combustion.

(b) In case of initial temperature at 250°C(Test No.2 & 3)

A small particle of fire due to sodium scattered immediately after sodium was loaded, but it is attributable to a part of sodium which was spurted in the form of fog and got fire because

the inlet for sodium in the combustion dish was too small, and it was avoided by improving the inlet for the later test.

The generation of firing spot and its expansion were the same in phensmenon as that at 500°C, but in case of sodium unrefined, it was observed that the firing spot sometimes expanded move quickly and burned more fiercely than that in case of loading temperature at 500°C.

Moreover, once it got fire and ablaze, the combustion expanded in itself by heat of combustion reaction, and it was found to be of little influence on the phevomenon of burning expansion due to initial temperature of sodium. Almost no difference was found between the combustion phenomena of Tests No.2 and 3, but after the end of fire, combustion products of No.3 were shaped more irregularly.

(c) In case of other temperature

When unreacted sodium was withdrawn from the combustion dish, it was tried to observe the use of gravitical with drawal at 230°C and ignition phenomenon in air. As a receptable had not been preheated, it cooled rapidly, but something in the form of bubble due to the covering of oxide was generated at the point of sodium dropping, and that part of polyhedron was ready to burn. However, it was easy to take off the product in the form of bubble, and then the treatment in case of getting fire was also very simple. Apart of liquid sodium in a receptacle got fire and burned, but when the surface in question was skimmed, it ceased to burn, and about 7kg of sodium (about 50mm in depth) was relatively safely cooled and solidified in about an hour and a half.

Further, when sodium was withdrawn in the same condition except for 150°C, no product in the form of buble, and no fire was generated and it was safely cooled and solified in about an hour.

3.3.2 The effect of initial oxygen concentration

(a) Oxygen Concentration at 21v/o

Refer to (a) in 3.3.1

(b) Oxygen Concentration at 15v/o and 11.2v/o

Even though sodium was loaded relatively slowly into the combustion dish in case of 15v/o, the sight in the vessel became zero due to

severe fuming before the expected liquid level of 150mm was attained. And also, the state of ignition showed a irregularity in its strength, and it was not clear to identify the end point of the ignition combustion. The combustion phenomenon itself did not show any difference from the case of 21v/o. In case of 11.2v/o, some firing spot and fuming were observed on the surface on the way of sodium loading. However, no combustion expanded rapidly but it proceeded slowly. Time required to reach zero sight in the vessel was the longest in the series of tests, and it was observed that burning sodium deposited on the inner wall of the combustion dish and creeped up.

Moreover, the test was carried out by assuming relative humidity of 35% at 20°C, and as compared with the tests in the previous year (9.6v/o, 70%RH, 500°C : No combustion to be observed), the generation of initial firing spot is attributable to the fact that the relative humidity was of half and the impurity content in sodium such as calcium and so forth was higher.

3.3.3 The effect of gas temperature

When air temperature in the vessel proper was elevated to 110°C in average and sodium was burned in the combustion dish, the generation of firing spot was similar to the tests in the previous year. However, time required to obtain the combustion over the whole surface as firing spot expanded, was relatively longer as 2.5 minutes and the aspect of the combustion was moderate.

3.3.4 The combustion open to the air

During sodium loading, liquid level went up along with a white film of oxide, firing spots generating at 4 to 5 places. They spreaded over the whole surface 2 minutes later, combustion products creeping and rising up to the edge of the combustion dish. After 5.5 minutes, sodium overflowed to the outside of the combustion dish due to capillary phenomenon through the products. The color of the products was changed from yellow to white one hour later. After four hours, the fire was extinguished naturally and sodium the combustion dish was of from 180 m/m to ca. 60 m/m in depth, that is a third of the level as compared with that immediately after loading, and was covered with a hard crust (consisted of

sodium carbonate and so on). This is the most different phenomenon to be observed with the combustion in the closed vessel. Also in the crust sodium remained as a mixture with sodium oxide and so on after it was closed in from air and ceased to burn due to lock of air. It took much more time to wash out than the washing after the combustion test in the closed vessel.

Further, there are two cases in which sodium was burned in air, that is, in cases of A (75%RH, 29°C) it got fire at 280°C(see Photo 3.8), and in case of B (73%RH, 23°C) at 250°C (See Photo.3.9.) and temperature went up to 400°C after 10 minutes.

3.4 Combustion Product

The product generated on the combustion dish after the test in the closed vessel was the same in appearance as that in the test of the previous year. Also dendrite of sodium was apparently formed at the upper part of the inside of the combustion dish. A part of it was taken out and shown in Photo 3.10.

§4 Combustion Rate of Sodium in the light of Variation in Oxygen Concentration

4.1 Purpose

After the combustion rate of sodium was obtained from the measurement of the decreasing rate of oxygen concentration, its relationship with initial oxygen concentration (v/o), initial temperature of sodium, humidity, initial air temperature and the combustion area was investigated.

4.2 Method of Measurement

As it was the same as the previous report, it was omitted here.

4.3 Combustion Rate

Results of measurement by the method stated above were shown in Figs. 4.1 to 4.7. In this test, the calculation of the combustion rate was obtained from the point where the combustion rate became liner, since it was small during initial five minutes. Whether the phenomunon appeared or not was dependent on the test. It is thought that this depends on the condition of sodium loading into the combustion dish (loading rate). The results obtained from the data treatment in a similar manner as the previous report are shown in Table 4.1

4.4 Consideration

4.4.1 Initial Oxygen Concentration and Combustion Rate

The measured values under the same condition of S/So = 0:85 were plotted with the relationship of the previous report between initial oxygen concentration and the conbustion rate in Fig.4.8. Referring to Test No.6, under this test condition, that is at 11.2% of initial oxygen concentration, firing spot was observed but its increment was very low, then the temperature of the combustion dish went up to 500°C after 1 or 2 minutes. It is deemed that it would be, in fact,of lower value than that of Tests No.6 and No.7 of the previous report. In the Figure, the plot was drawn from obtaining values approximately corresponding to S = 0.15m^2 by using the relationship between the combustion rate and S/So, since the combustion area was different and it could not be plotted directly on the graph.

It is assumed that the combustion rate increases exponentially as initial oxygen concentration increases, and also that there is a limit around 11.2% of initial oxygen concentration as to whether firing spot would be generated or not.

4.4.2 Initial Sodium Temperature and Combustion Rate

The relationship between initial temperature of sodium and the combustion rate is illustrated in Fig. 4.9. Sodium used for each of No.1, No.2 as well as of No.3, No.4 are of the same kind respectively.

It is unable to say quantitatively on the basis of the test results, but was clarified that the combustion rate depended on initial temperature of sodium, and that it was remarkably affected by the purity of sodium.

4.4.3 The Effect of Gas Temperature

The test was carried out while air temperature in the vessel was heated up to about 100°C. The combustion rate obtained from this test was 0.493kg/m^3/min and almost the same as that in case of other normal tests.

It is assumed that the convection in the vessel was not disturbed in this test.

4.4.4 Oxidation velocity at the End of Sodium Fire

As stated above, when sodium fire occurred in a closed system,

oxygen in the system decreased apparently in zero order reaction. However, at the end of the fire, the decrease rate of oxygen lowered extremely and the rate of lowering is confirmed as in the first order reaction. (Cf. Table 4.2).

When firing spot is present on the exposed surface of sodium, ascending, current is tremendous in the system due to the reaction heat with the combustion, accordingly oxygen can be supplied by descending current. However, when firing spot can not be present any longer, the surface temperature of exposed sodium decreases, by heat transfer from sodium loop? to the vessel as well as by radiation from the sodium surface to the inner surface of the vessel exposed to gaseous phase, and as the velocity of ascending air current decreases, the supply of oxygen also decreases. In effect, the surface temperature of sodium has decreased at the rate of 10°C/min. Never the less, the surface of sodium will remain at high temperature and the convection will continue, though the extent of violence is inferior to that at presence of firing spot. Then, it is assumed that oxygen in gaseous phase continues the reaction not only by the effect of diffusion but by the contact with the surface of sodium due to the convection. The fact is that which had been observed in the reaction without the generation of firing spot [The previous Tests No.1-6 and No.1-7(sodium temperature at 500°C constant)].

The homogeneous first order equation is given, when the concentration of chemical material in question is C, as follows:

$$\frac{d[C]}{dt} = Ki\,[C] \quad \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

where Ki has a dimention of $[T^{-1}]$ and is a constant independent of initial concentration.

Because the system treated here is heterogeneous, and moreover is changeable with the velocity of feed oxygen, the surface temperature of sodium, the surface area and the surface condition, it is impossible to be defined by the simple mathematical treatment at all. The review on the facts observed in the test will be done in section 7.2.

§5 Calculation of Heat of Combution Reaction

5.1 Purpose

By giving a process consisted of sodium system, it is desired to calculate the heat of combustion reaction from the amount of energy change in the whole process as well as the combustion rate thermodynamically from the rates of energy and density change of gas molecule in the vessel. Here, the decrease of gas molecule density in the vessel corresponds to the decrease of oxygen molecule, that is, the velocity of oxidation combustion, if the gas in the vessel is considered to be as ideal gas.

Measuring points of the pressure and the temperature are shown in Fig. 5.1.

5.2 Calculation Method

As the calculation method, fundamental equation and physical properties data have been described in detail in "Model Test of Na Pool Fires-No.1", they are not reiterated here on purpose.

5.3 Results of Measurement

Results of measurement for pressure and temperature are shown in Figs. 5.2 to 5.8. In the Figures each temperature represents an average temperature with the total weight of the system. As clarified in the Figure, the maximum values of each of temperature and pressure (some differences are seen due to each test conditions) are 200°C at most and less than 0.22kg/cm^2. These values are much lower than the analysis results of 620°C for temperature and 1.7kg/cm^{2}G for pressure which were obtained by Code [NAFIRE], it being used for safety analysis. This depends on the differences of models, but will be separately reported in detail.[3)]

5.4 Calculation Results and Review

5.4.1 Heat of Combustion Reaction

(1) Heat of Combustion Reaction

Results of calculation as to heat of combustion (reaction) are shown in Table 5.1. Also the calculated values for heat of combustion (reaction) on the basis of the assumption that combustion (reactions) in all proceed following the equation, are also shown in the above table.

$$2\,Na + \tfrac{1}{2}\,O_2 = Na_2O + 104\ Kcal/mol \qquad (5.1)$$

Although the existence of four kinds of sodium oxide has been recognized, two species of Na_2O and Na_2O_2 are formed abundantly in the reaction between sodium and air. In these reaction, Na_2O is formed at first, then it is further oxidized to Na_2O_2 when oxygen is present in excess. In fact, in the initial period in which there are plenty of oxygen, Na_2O is formed partially, and then, it is deemed, it is gradually reduced again. Therefore it will be able to consider as if only the first reaction mainly proceeded.

On the other hand, according to the observation results by naked eye and video-tape recorder as well, at least in the early period there prevailed a quite different (combustion) reaction from that in the previous report, and after the end of (combustion) reaction it appeared that oxide in quantities was floating on sodium pool and appeared quite different as compared with the mirror state in the previous report.

Here at least as to the former it is attributable to potassium content that was present in this case as much as about 1%, as compared with 0.1% in the previous case, which was the most reactive in sodium metal.

Further, there exists a small quantity of moisture in air, but it is so small that it has a little effect on the total combustion (reaction).

It may be allowable to calculate the heat of combustion (reaction) for sodium-air reaction in the closed vessel, assuming that only it proceeds with the equation indicated as (5.1), even in the presence of potassium to the extent of 1%.

(2) Thermal Balance

Among the heat generated by the combustion (reaction), about a portion of 50~70% of it may be transferred to the gas and the autoclave at the end of combustion (reaction). The rest of 50~30% may be transferred to sodium pool and the combustion dish for sodium (See Table 5.1). In case of sodium pool fire, about 50~30% of heat from the combustion (reaction) may be reserved in the side of sodium pool, because the combustion of sodium is the surface combustion and thermal conductivity of sodium is greatly

larger than that of other liquid fuels. Moreover, its oxide is heavier than that of other liquid fuels and scatters very limitedly and the most of them moves to the place of lower temperature.

Now let us consider the process of heat transfer to the gas and the pressure vessel from reaction zone of combustion. The details will be separately reported,[3] but speaking of main points, given 1500°C of temperature for firing spot and 50% for distribution ratio on the combustion surface, 80% of heat transfer to the pressure vessel may be governed by reaction. The rest of 20% may be transferred to gas by natural convection from liquid surface of sodium and flame, scattering of oxide or by radiation absorption by aerosol. The process of heat transfer is an important element to rule pressure vessel, so a seperate report[3] will be presented as for the detailed consideration.

Since Code [NAFIRE][2], being used for safety analysis previously, does not take account of residual heat of combustion in the side of sodium pool and heat dispersion by radiation, it is found to be a very safer model.

(3) Temperature Distribution

The temperature distribution is mainly governed by the shape of the container vessel and the combustion dish (See. Figs. 5-9 to 5-15).

Since it governs the natural convection of gas in the vessel, the combustion rate, scattering and deposition of oxides to the inside of the vessel as well as eventually the heat transfer to the inner surface of the vessel, it is a very important element in the light of the pressure response in the vessel.

As to this, it will be separately reported.[3]

5.4.2 Rate of Combustion Reaction

The combustion rate was obtained thermally from the variation rate for the density of the gas in the vessel and for energy in the whole system as well (See Figs. 5-16 & 17). The results are shown in Table 5-2. As shown in the table, there are large differences between this and the combustion rate obtained from the variation rate of oxygen concentration in the vessel, but this will be considered in the next chapter.

§6 Comprehensive Consideration and Conclusion

6.1 Effect of Sodium Metal

It has not been considered of peculiarities on the phenomena of the combustion due to the difference in sodium purity from the view point of various experiences and facts. For instance, sodium which contained pottassium in a little excess and was of technical grade, was used for the combustion test and also the extinguishing agents test, especially remarkable luminous phenomena was not observed. In the previous test sodium of technical grade and prepared by Castner process (electrolytical method of NaOH) was used. However in the light of this test, when the sodium surface without oxide film began to be oxidized by contact with air, not only the formation of moss-like oxide proceeded rapidly but also the formation of firing spot for its source became extremely faster, it was generally observed.

Tests No.1 and 2 were done as indicated in Table 3.2, by using sodium containing potassium 10 times as much as 0.1% in normal case (and in the previous test as well). From Test No.3 on, sodium of technical grade and prepared by Downs process (Electrolytical Method of NaCl) was used and the metal contained calcium of 290 ppm, 10 times as much as 24 ppm in the previous test. The temperature at the bottom of the drum was kept at 100~120°C, there was a segregation of calcium in excess because of more than its saturated solubility (110 ppm at 100°C), and sodium containing high percentage of especially rich of calcium seemed to have been loaded. On account of the structure of the apparatus, sodium used for Test No.3 calcium had a possibility of increasing calcium content in particulars, and it is supported by the observation through the viewing window. On the contrary, Tests No.6 to 8 might be done by using sodium which contained less calcium than 290 ppm. These are likely the reasons for a greater combustion rate as shown in Table 5.2.

6.2 Combustion Rate in the light of variation of Oxygen Concentration.

Like the previous test, the combustion rate, at first, was obtained from the variation of oxygen concentration in air. The results are, as shown in Table 4.1 and Figs.4.1 to 7, of relatively small values. This does not correspond to those facts such as the start of violent combustion, short time for luminous combustion, the density and the

combustion rate expected from heat content level, which were observed through the viewing window (See Table 5.2).

It is considered that abnormality as compared with the previous test has been caused in measuring conditions owing to some unknown cause. The abnormality in apparatus for oxygen measurement is hardly considerable because its caliburation has been carried out. Also, the final concentration of oxygen of ca.1v/o, the same as that of the previous test, could be accountable for the normality.

The cause to be accountable for will be the variation of the convection state in the gaseous phase in the reaction vessel.

Since the number of thermocouple for the temperature measurement in the gaseous phase were increased from 12 pieces to 30, the disturbance to the convection has taken place due to stainless foil in 30 mm square (radiation protection plate) which fitted at the tip of them, and the decrease in oxygen became likely to delay around the upper part of gas sampler. This is supposed from the fact that the sign of the temperature difference between thermocouples G-16 and G-19 in Fig. 5.1 is inverse as compared with that between thermocouples T-32 and T-21 in Fig. 5.9 in the previous test.

Accordingly we like to consider the value calculated and shown in the next section as more reliable. Apparently since Figs. 4.1 to 4.7 presented attenuation curves almost as the same as those in the previous report, it was unable for us to make any amendment on the way of the test.

It is supposed that the combustion rate became so much less because the oxygen distribution was unhomogeneous and oxygen close to the surface of combustion became smaller than the average.

6.3 Combustion Rate in the Light of Variation on Temperature and Pressure

In this test the detailed temperature distribution and its variation as time elapsed were measured by increasing measuring points of temperature more than in the previous test. A separate planning is under way in order to analyse fully the data obtained, and to complete a model to be able to extrapolate to the practical scale such as an experimental reactor. A part of the analysis is shown in chapter 5 in this occation.

According to the analytical results obtained, as shown in Table 5.2,

the combustion rate showed in general greater valves than that obtained from oxygen concentration.

However, the value calculated by density basis coincides very well with those by heat of combustion basis, both of these showed a linearity in zero order reaction with very good approximation.

Further, as manifested in Table 6.1, the time when the end of luminous combustion was observed is in good coincidence with the time when combustion rate changed from zero order reaction to the first order one, using values calculated above.

Incidentally in such adiabatic system as this test, it was already clarified in the previous report that attenuation velocity of oxygen could be calculated in quite good approximation, using measured values on temperature and pressure. This time measuring points for temperature were further increased, the precision is supposed to be sufficiently improved.

6.4 Reaction Zone of the first Order and Luminous Combustion

As mentioned in the previous section, the variation in oxygen concentration showed a large delay in time and did not show any average in concentration, it is supposed, analytical results as to the tests in Table 4.2, that is No.II-1～ No.II-7 could not be reliable.

Accordingly the reason is considered to be clarified which accounts for the high value as 10～15% of oxygen, different from the value in the previous report, at the time when luminous combustion came to end.

It can not be expected to obtain oxygen concentration near the correct liquid surface from correction, but it would be supposed to be around 5v/o as shown in the previous test results.

It is interesting that there is a fairly good coincidence between the end time of luminous combustion and that of zero order reaction in the light of heat of combustion and variation in density.

It would be based on the reasons such as preheating etc. that in Tests No.II-5 and II-6 they did not show any good comformity.

As to the velocity coefficient K_1 of the first order reaction (Table 4.2) it will be of little value even if that is obtained by the analysis on the data of this test.

6.5 In Respect to Results from the Previous Report

As is clear in Table 5.2 of the previous report, each of the combustion

rate of sodium obtained from the variation in oxygen concentration, the variation in the density and the calculation in heat of combustion showed fairly good coincidence with each other. Therefore the various conclusions proposed in the previous report are not required to be corrected.

Furthermore, on the basis of the precise measurements of the temperature, increasing measuring points and its analysis, it becomes possible to make precise correction interpolately in respect to the temperature distribution and to make discussion with much higher in precision.

As good coincidence with each other has been reached, it is not necessary to change the conclusion, but it is desirous to report the results of recalculation corrected in the report "On the analysis of the combustion mechanism".[3]

§7 Conclusion

(1) The test apparatus was almost the same as before, except that measuring points for temperature in the gaseous phase were increased to 30 from 12. Also other measuring points for temperature were increased to 30 from 16. Therefore the precision in measurements for the temperature distribution and its variation went greatly high. The combustion rate based on each of heat of combustion and of density which were obtained therefrom showed a good linearity of zero order reaction in respect to the time required to end the blazing combustion. Both results showed a good coincidence and it is possible to make more reliable analysis than expected. It was found to be much more linear than from the variation measurement of oxygen concentration liable to segregate.

(2) Sodium used for the test was of technical grade and most of it was prepared by Downs process, though it was, in the previous report, of technical grade and prepared by Castner Process.[1] Because this contained 290 ppm of calcium 10 times more than that in the previous test, the following results were obtained: The almost same results were obtained for the metal containing 1% of potassium 10 times higher than that used for Tests No.1 and 2, that is, under the test condition of 500°C at initial, 0.15m^2 of the combustion area, 0.085 for S(combustion area)/ So (cross section of the container vessel), the combustion rate obtained became 0.9kg/m^2, min. for the metal in this test as shown in the Tests No.1 and 4, compared with 0.5kg/m^2, min. from Fig.4-11 in the

previous report.

(cf.Table 5.2: Combustion rate based on heat of combustion and on density)

(3) The combustion rate in the light of variation in the oxygen concentration became greatly smaller than that from other method. It is assumed from such matters as observation results of the surface and the distribution state of temperature etc, that these were caused by the disturbance of the convection and by insufficient mixing in the gaseous phase, each being due to the increment of measuring point for temperature in the gaseous phase.

(4) Since in the analysis of the previous test, three kinds of the combustion rate had almost coincide with each other, the various conclusion based on the analysed data obtained mainly from the variation in oxygen concentration will need not change. Especially relationships with S/So was shown in Table 7.1 and the curve (real line in the figure) shown in the previous report as the most probable value would remain to be of dependable.

(5) Further, as stated in (1), with detailed data as to the temperature distribution, it became easier to assume interpolation in regard to the previous data and also to improve in precision for analysis. And also, since it became easier to analyse the combustion mechanism, it is under way to consider how to obtain anequation feasible to extrapolate for experimental reactor in scale.

§8 Acknowledgement

We are grateful to Mr. Yoichi Suzuki and Mr. Minoru Fukushima of Power Reactor & Nuclear Fuel Development Corporation, who had been helpful to the practice throughout the test. Further we appreciate very much the collaboration rendered from other members of Na Laboratory, mentioned here, especially of Messrs. Takashi Sudo and Toshiaki Kumada, the analysis by Analysis Center, JAERI and Miss Yoko Tominaga and Miss Junko Sato who have completed the arrangement of huge amount of data and its calculation steadily.

§9 Reference

(1) Model Test of Na Pool Fire - No.1 by FURUKAWA et al, Dec. 1968

2) " NAFIRE - Code for the analysis of the reaction between Sodium and air" by TASAKA et al JAERI memo No.3181

3) "Mechanism Analysis of Na Combustion and Fire" by FURUKAWA et al. (Expected Completion in Dec. 1969)

Table 3.1 Test Condition

Test	2	3	1	4	7	5	6	8
Initial temperature of sodium (°C)	250				500			
Initial oxygen Concentration(V/o)	21		21			15	11.2	21
Combustion area(m^2)	0.15		0.15		0.15	0.15	0.075	
Liquid depth (mm)	150		150		150	150	150	180
Sodium quantity(ℓ)	22.7		22.7		22.7	22.7	11.3	13.5
Humidity (Relative at 20°C %)	68	74	75	68	70	70	3.5	75
Absolute humidity (g/m^3)	11.7	12.8	13	11.7	12.1	12.1	6.0	1.3
Others					Air temperature 110°C			Combustion in open air
Sodium used	A	B	A		B		B	B

A Sodium used in the refining test loop (K content : 1%) (cf. Table 3.2)

B Sodium prepared by Downs process, of technical grade (99.85% pure) (cf. Table 3.3)

Table 3.2 Analytical Results of Potassium and other Metallic Component in Sodium(ppm)

	K	Fe	Ni	Cr	Al
Na in Melting Tank	0.87 (%)	9	<1	<1	4
Na in Drum for Na	1.2% (%)	6	<1	<1	38

(Flame photometry, colorimetry) Analysis Center, JAERI

Table 3.3 Analytical Results of Na (ppm)

This test	Na	K	Cl	Ca	Si	Fe	V	Mg	Mn	Al	Cu	Ni	Cr
B in (Table 3.1)	99.85 (%)	200	49	290	10	<10	<10	<10	<10	<10	<10	<10	<10
Previous Report	99.6 (%)	1800	40	15	15	15		25		15			

Table 4.1 Combustion Rate under Various Conditions

Test No.	Initial Oxygen Concen. (v/o)	Exposed Surface of Na $S(m^2)$	Liquid depth of Na 0 (mm)	Na quantity loaded (l)	Amount of initial vapor (g/m^3)	Exposed surface / Cross section of vessel (S/So)	Combustion rate (Reaction velocity) kg/m^2-hr	kg/m^3-min	lb/ft^2.hr	lb/ft^2-min
1	21	0.15	150	22.7	13.0	0.0849	64.7	1.08	13.3	0.221
2°	21	0.15	150	22.7	11.7	"	27.3	0.455	5.59	0.093
3°	21	0.15	150	22.7	12.8	"	20.7	0.345	4.24	0.071
4	21	0.15	150	22.7	11.7	"	28.7	0.478	5.88	0.093
5	15.1	0.15	150	22.7	12.1	"	11.1	0.19	2.27	0.038
6※	11.2	0.075	150	11.3	6.0	0.0425	17.7	0.29	3.62	0.060
7*	21	0.15	150	22.7	12.1	0.0849	29.6	0.493	6.06	0.101

※ Temperature of combustion dish has been kept at 500°C

* Initial gas temperature > 100°C

o Initial Na temperature : 250°C, others : 500°C

Table 4.2 Transfer Time to the First Order Reaction

Test	Initial temp.	Commencement of first order reaction t'	O_2 Concen.	$T_{\frac{1}{2}}$	k_1 $0.693/T_{\frac{1}{2}}$
I-2	500	26 (min)	5 (%)	8 (min)	0.086 (min)
I-3	500	27	5	6	0.115
I-4	500	23	3.7	15	0.046
I-5	500	19	6	6	0.115
I-6	500 const	0	5	22	0.0314
I-7	500 const	15	8	18	0.0385
I-8	500	25	8	7.5	0.0925
II-1	500	16	5	7	0.095
II-2	250	25	6.4	9.5	0.073
II-3	250	25	11.5	10	0.0693
II-4	500	24	12	10	0.0693
II-5	500 const	25	12	17	0.0407
II-6	500 const	29	6.8	10	0.0693
II-7	500 (gas 110°C)	20	11.5	5	0.139

Table 5.1 Heat of Combustion Reaction and Ratio of Heat Transfer

	Initial oxygen concen.	Total heat of combustion		Ratio of heat transfer 2)	
		value measured kcal	value calculated 1) kcal	Na Pool Side %	Pressure vessel side %
1	21	5280	5750	51.9	48.1
2	21	4600	5750	42.0	58.0
3	21	4270	5750	34.8	65.2
4	21	4400	5750	41.1	58.9
5	15.1	3940	4150	52.8	47.2
6	11.2	3330	3100	31.6	68.4
7	21	4700	5750	57.7	61.3

1) $2Na+\frac{1}{2}O_2 = Na_2O + 104$ Kcal/mol

2) Value at the end of the combustion reaction in view of thermodynamics.

Table 5.2 Combustion Rate

Test	Initial Oxygen Concen.	Loading temp. of Na °C	Area of Na pool m2	Combustion rate kg/m2 - min		
				Heat of Combustion basis	Density basis	Oxygen concen. basis
I-1	21	500	0.075	0.98±0.07	1.72±0.26	-
I-2	21	505	0.15	0.50±0.03	0.58±0.10	0.51
I-3	21	520	0.15	0.57±0.02	0.68±0.03	0.45
I-4	21	500	0.30	0.31±0.02	0.47±0.04	0.36
I-5	21	505	0.15	-	0.68±0.04	0.62
I-6	5.2	470	0.15	0.12±0.01	0.11±0.01	0.08
I-7	9.7	475	0.15	-	0.16±0.02	0.13
I-8	21	495	0.075	0.91±0.07	1.23±0.09	0.85
II-1	21	470	0.15	0.89±0.04	1.03±0.09	1.08
II-2	21	300	0.15	1.05±0.10	(1.49±0.10)	0.46
II-3	21	250	0.15	0.87±0.10	(1.29±0.31)	0.35
II-4	21	475	0.15	0.86±0.03	0.69±0.09	0.48
II-5	15.1	490	0.15	(0.62±0.18)	0.31±0.01	0.19
II-6	11.2	460	0.075	(0.53±0.01)	0.57±0.03	0.29
II-7	21	460	0.15	0.75±0.03	0.76±0.04	0.49

Table 6.1 Combustion Time

Item / Test	Na temp. loaded (°C)	Initial Oxygen concen. (v/o)	Time required for completion of luminous combustion (min)	Time for zero order reaction of combustion			Oxygen concen. at the beginning of zero order reaction (v/o)
				Based on heat of combustion (min)	Based on variation of density (min)	Based on oxygen concen. (min)	
1	470	21	16	19	17	16	(6.5)
2	300	21	14	14.5	(17) *	25	13.7
3	250	21	18.7	18.2	(12) *	25	15.5
4	475	21	20	20	21.5	24	15.0
5	490	15.1	23.5	(27.5)**	37.5(?)	25	10.2
6	460	11.2	24	(35)**	30	29	8.2
7	460	21	21	21.5	23.5	20	10.6

Note: * Abnormality perceived in pressure measurement

** Continued preheating to 500°C

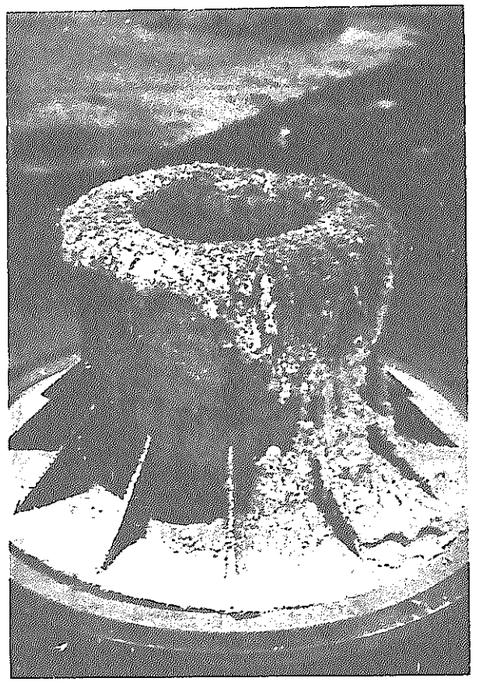


Fig. 3.1 Combustion Dish after Test in Test No.II-1

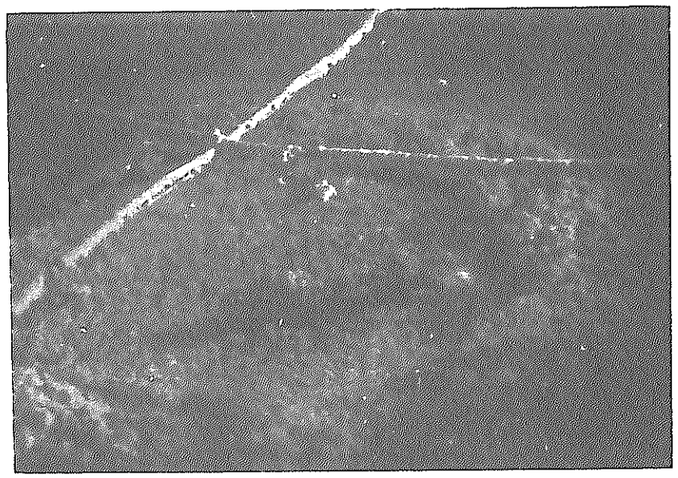


Fig. 3.2 Surface of the Combustion Dish Placed in the Container Vessel in Test No.II-2

Fig. 3.3 Surface of the Combustion Dish Placed in the Container Vessel in Test No.II-3

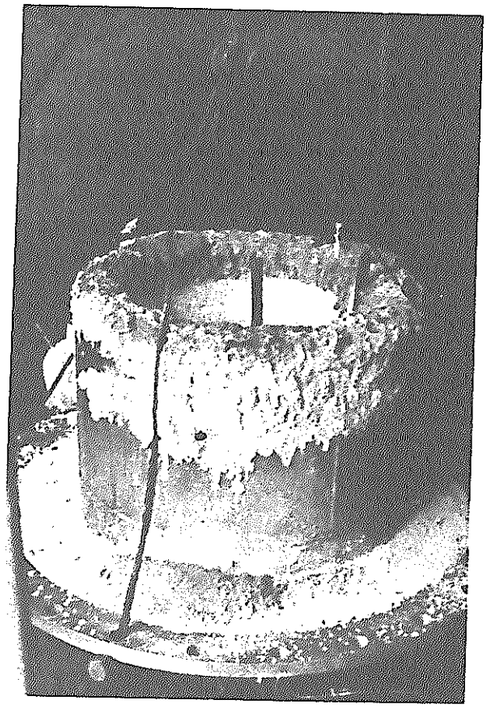
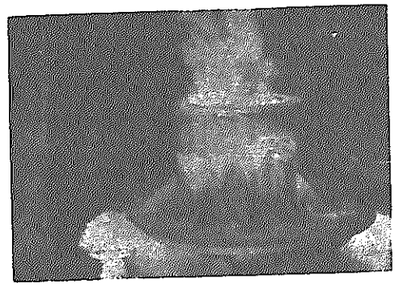


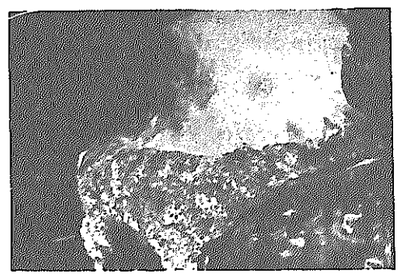
Fig. 3.4 Combustion Dish before Washing of Deposit Products in Test No.II-4

(a) Immediately after sodium



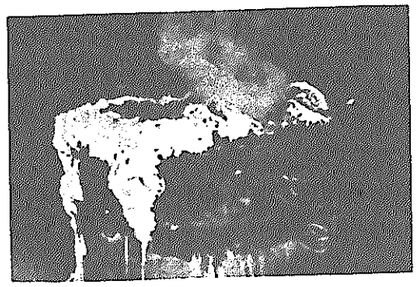
(b) After 2 minutes

(c) After 5.5 minutes

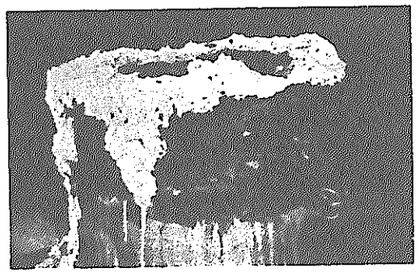


(d) After half an hour

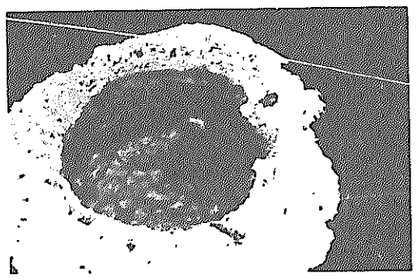
(e) After 1 hour



(f) After 2 hours



(g) After 4 hours



(h) Inside of the combustion dish after test

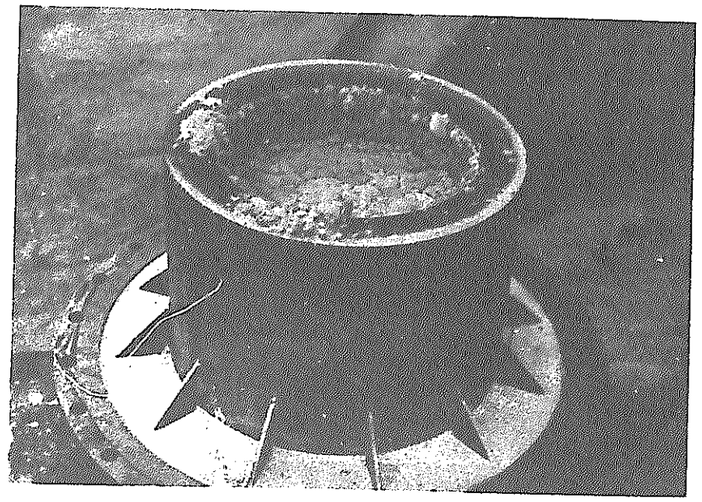


Fig. 3.5 Combustion Dish after Test in Test No.II-5

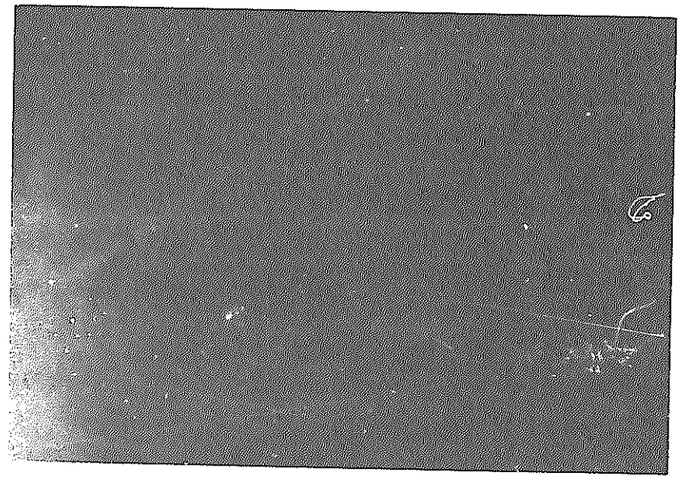


Fig. 3.6 Combustion Dish Placed in the Container Vessel after Test in Test No.II-7

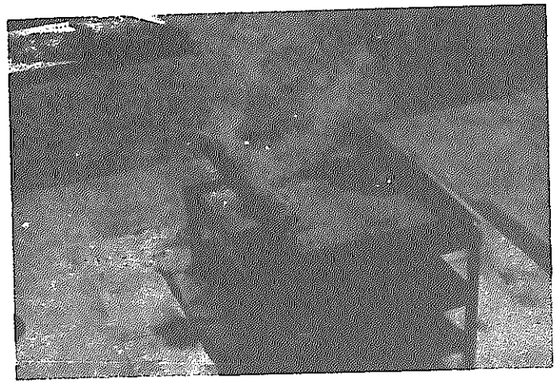


Fig. 3.8 Case A: Sodium Fire in Air

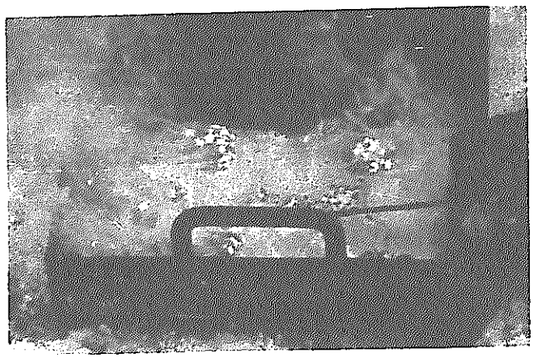


Fig. 3.9 Case B: Sodium Fire in Air

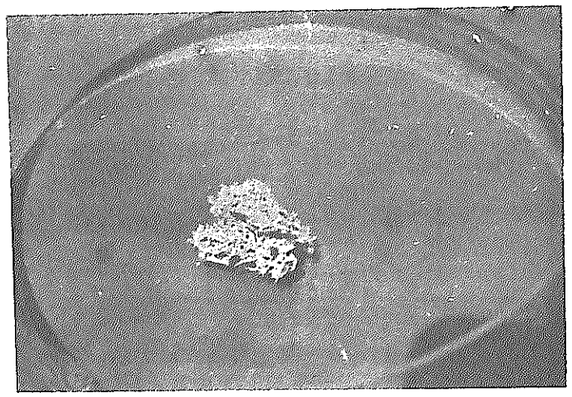


Fig. 3.10 Sodium Growth in Dendrite

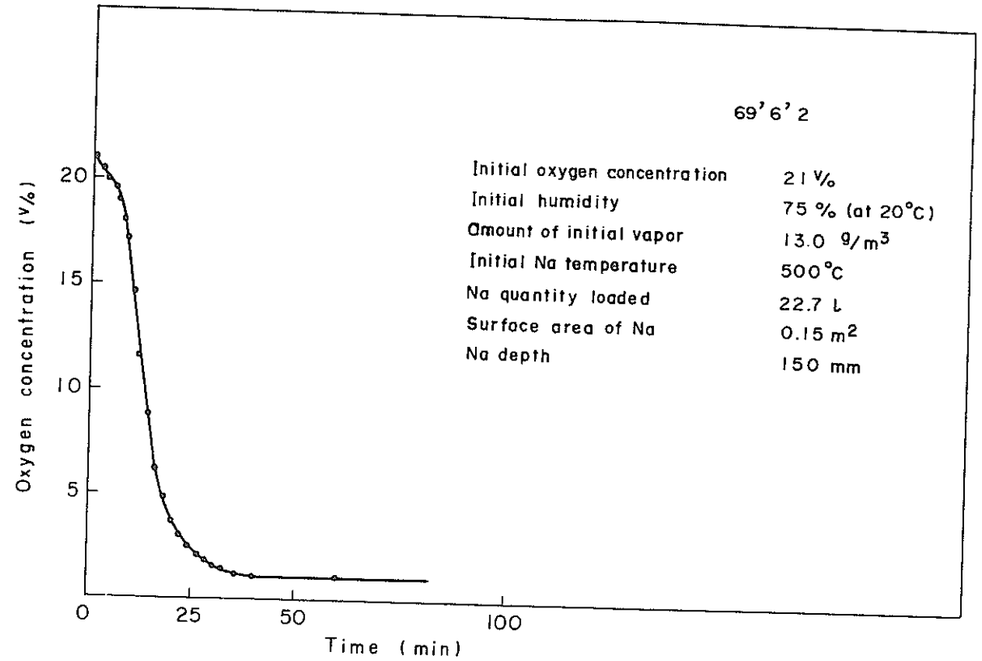


Fig. 4.1 Variation in Oxygen Concentration in the Course of Time for Test No. 1

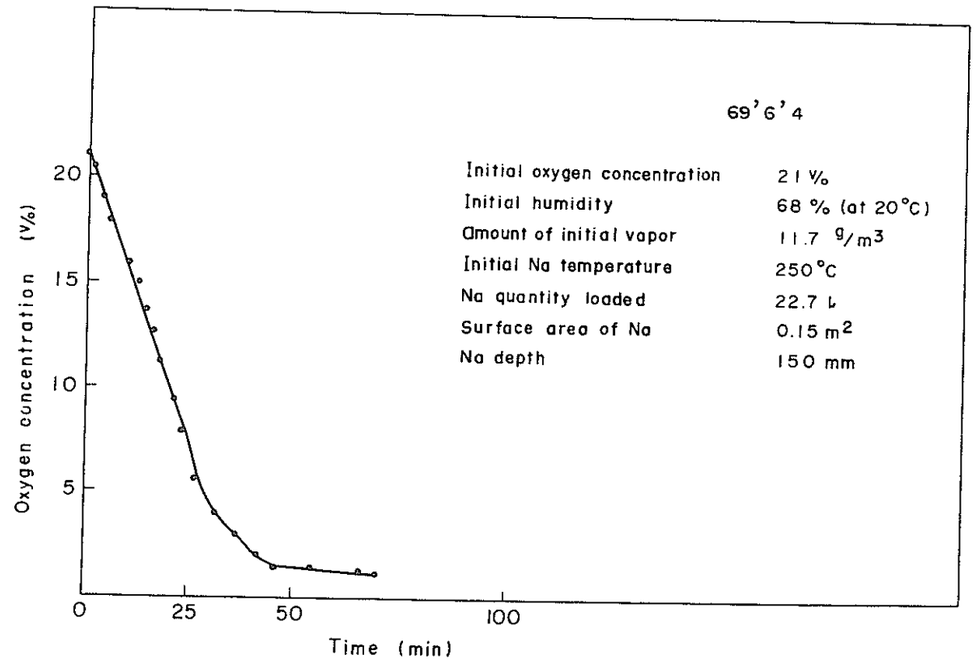


Fig. 4.2 Variation in Oxygen Concentration in the Course of Time for Test No. 2

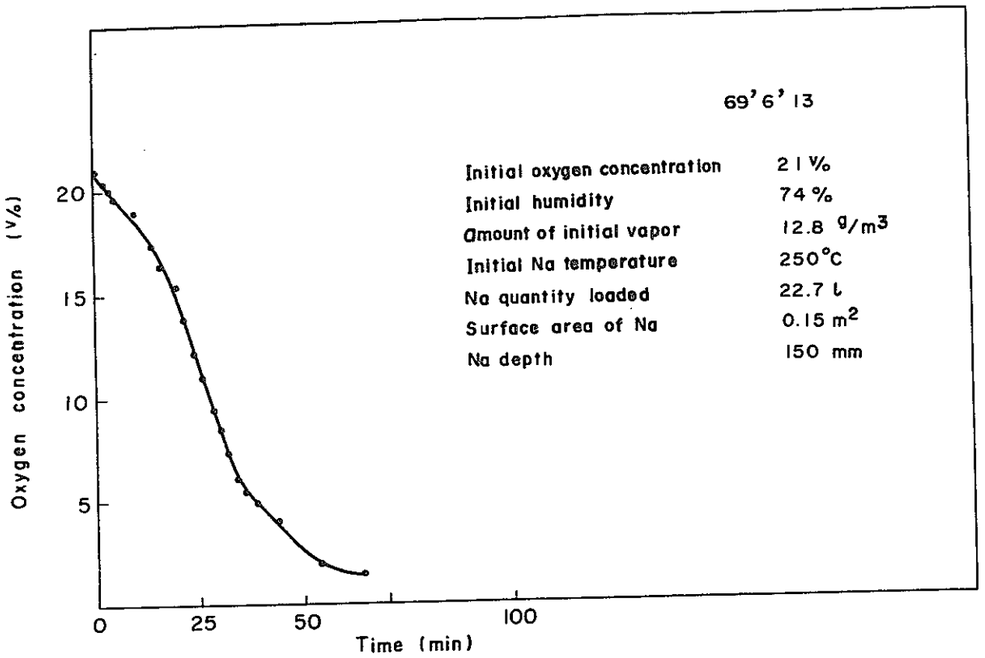


Fig. 4.3 Variation in Oxygen Concentration in the Course of Time for Test No. 3

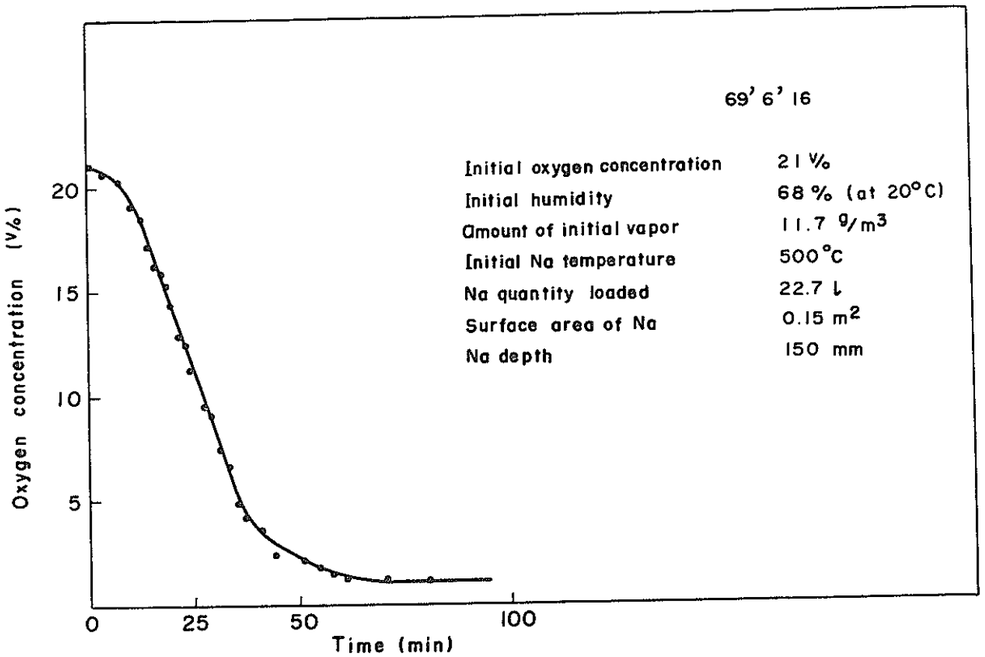


Fig. 4.4 Variation in Oxygen Concentration in the Course of Time for Test No. 4

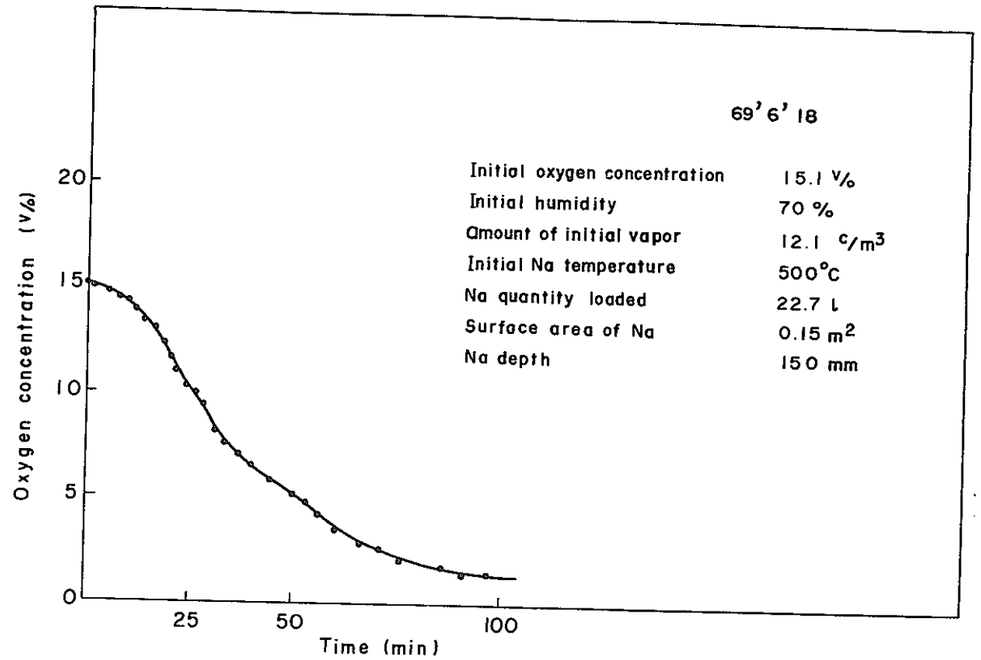


Fig. 4.5 Variation of Oxygen Concentration in the Course of Time for Test No. 5

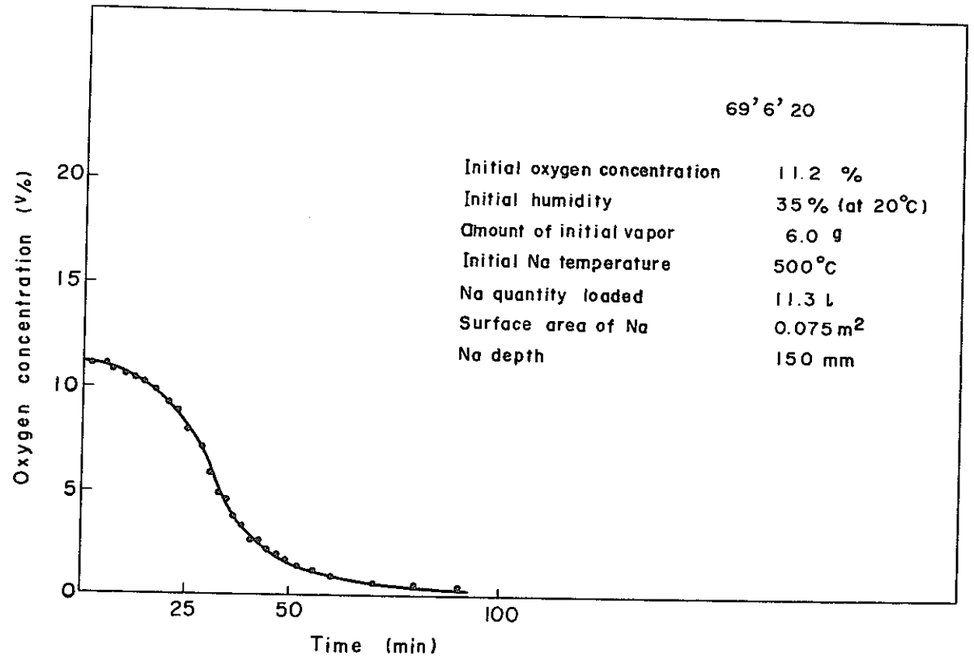


Fig. 4.6 Variation of Oxygen Concentration in the Course of Time for Test No. 6

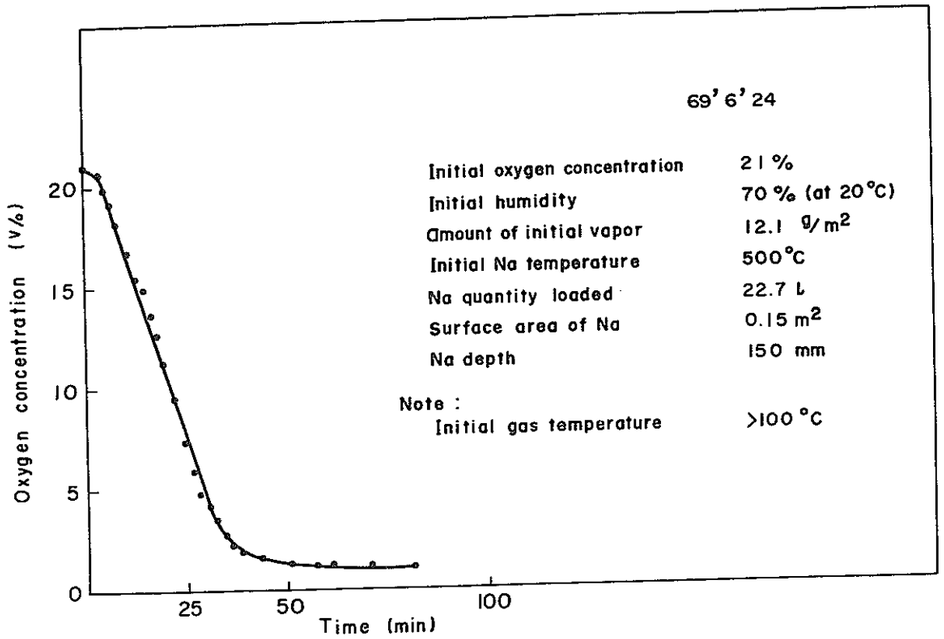


Fig. 4.7 Variation in Oxygen Concentration in the Course of Time for Test No. 7

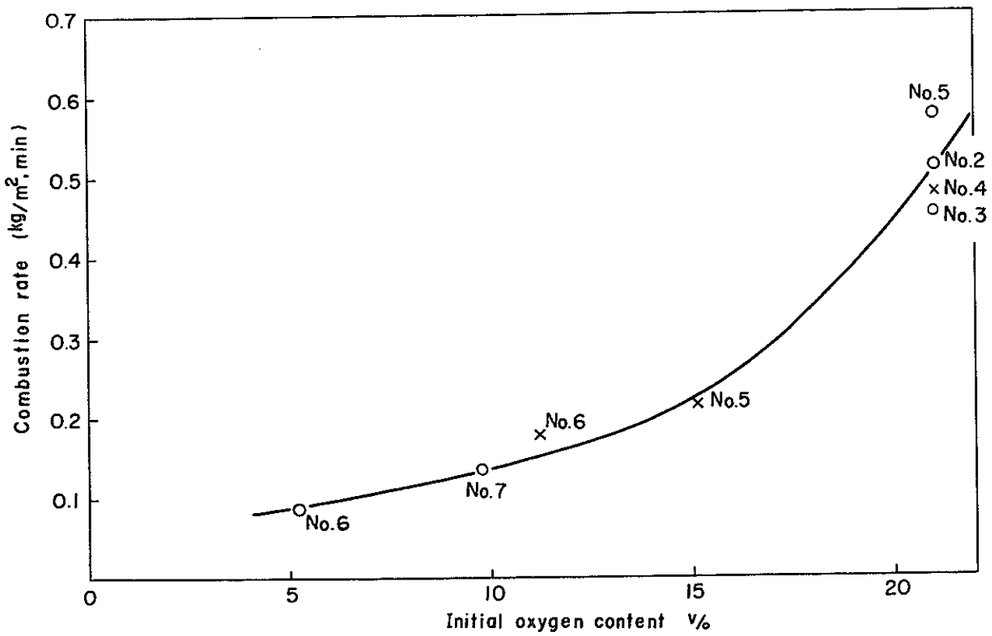


Fig. 4.8 Initial Oxygen Concentration and Combustion Rate

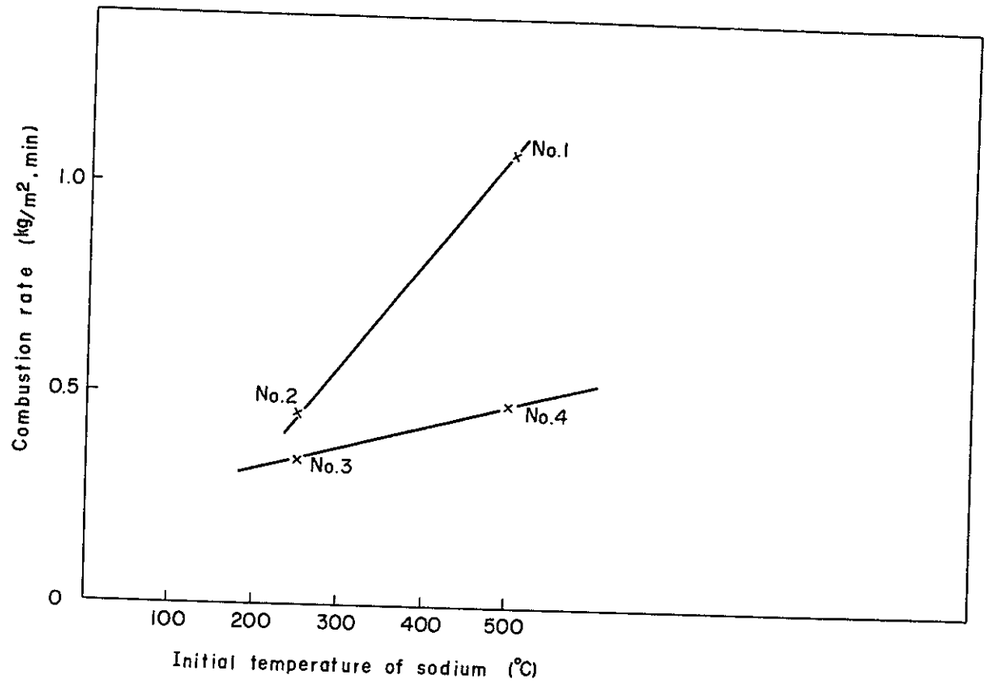
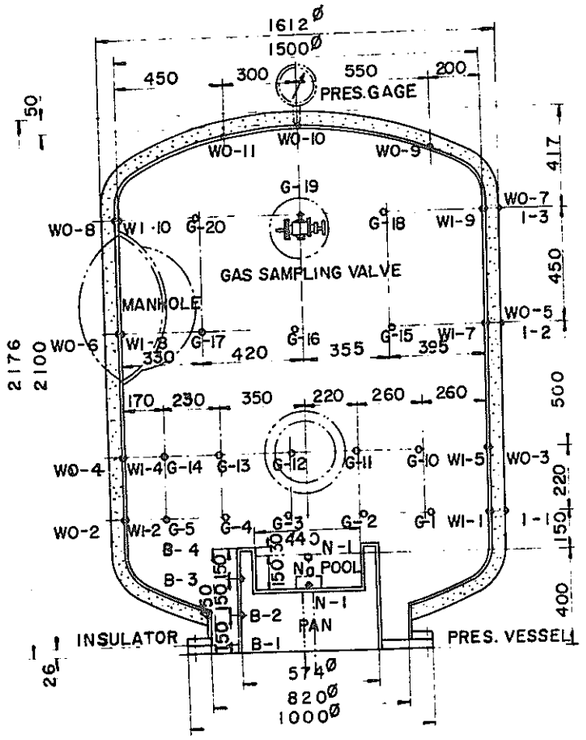


Fig. 4.9 Initial Temperature of Sodium and Combustion Rate



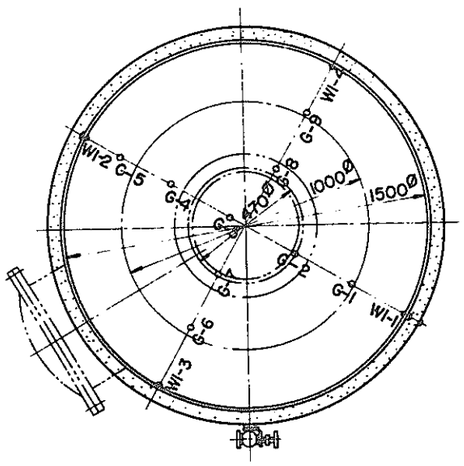


Fig. 5.1 Measuring Point for Temperature at Pressure Vessel

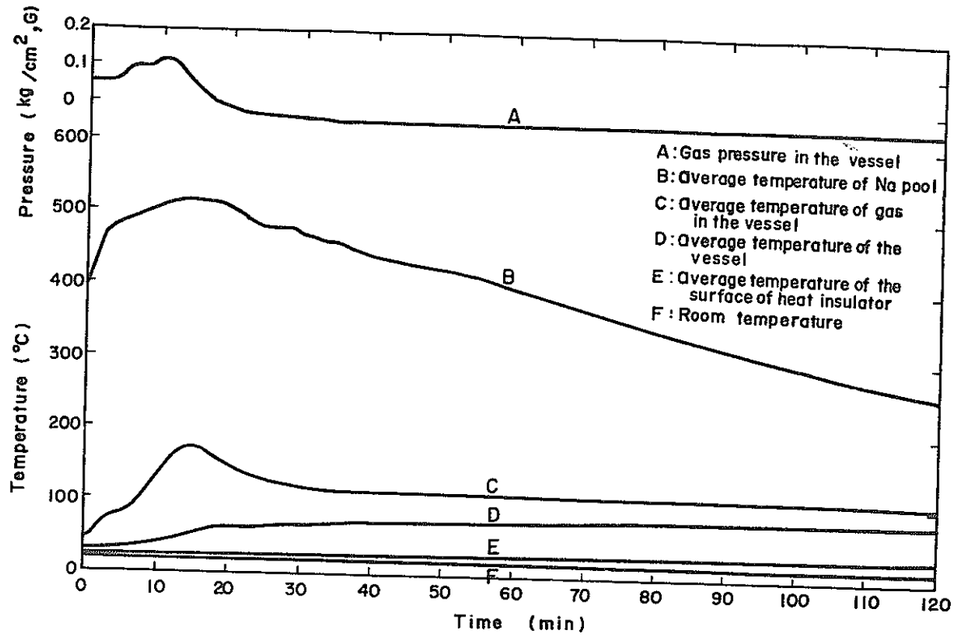


Fig. 5.2 Temperature and Pressure Response (Test No. 1)

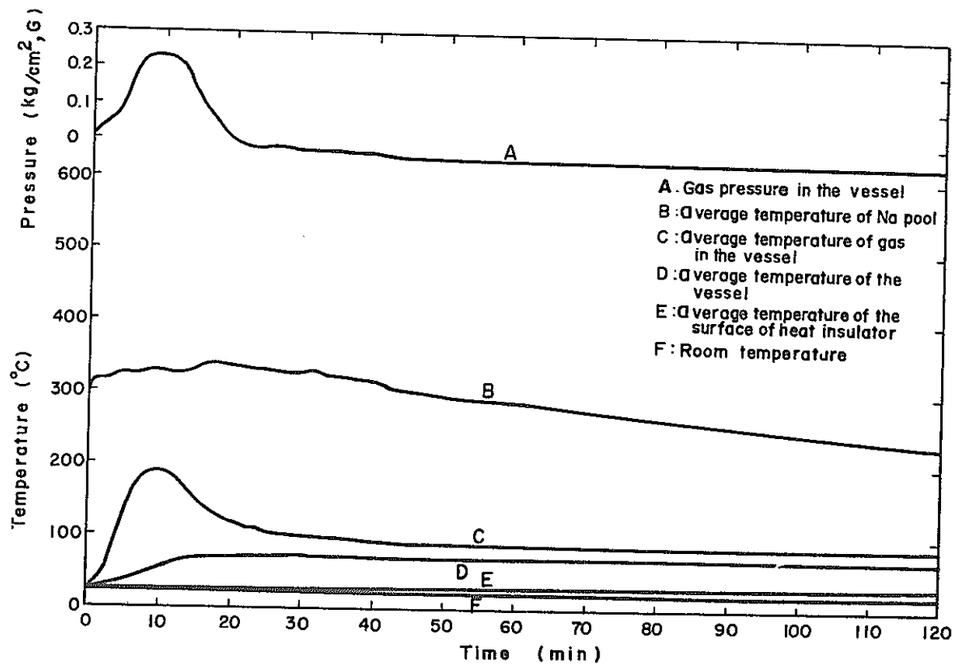


Fig. 5.3 Temperature and Pressure Response (Test No. 2)

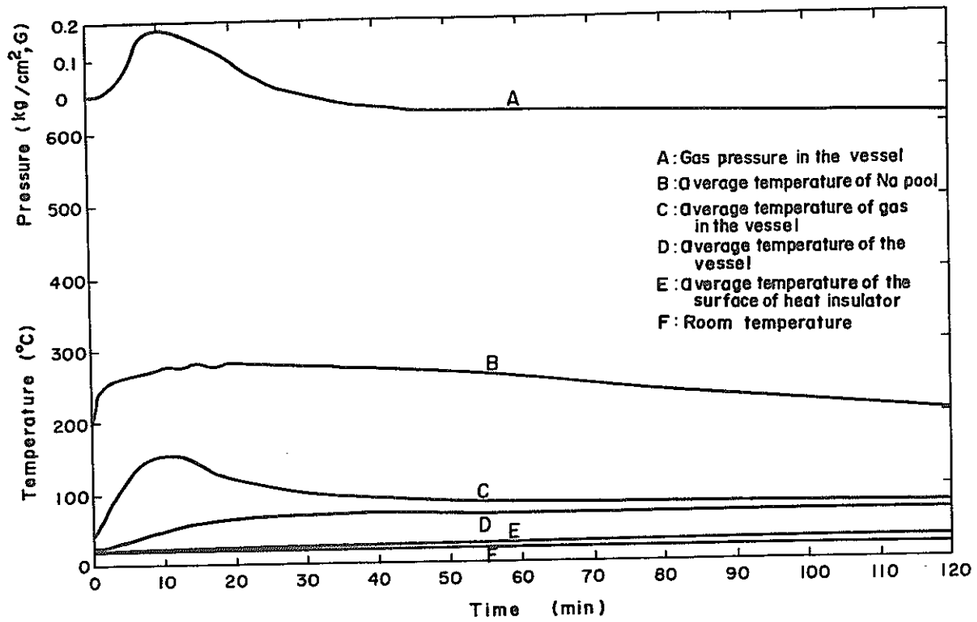


Fig. 5.4 Temperature and Pressure Response (Test No. 3)

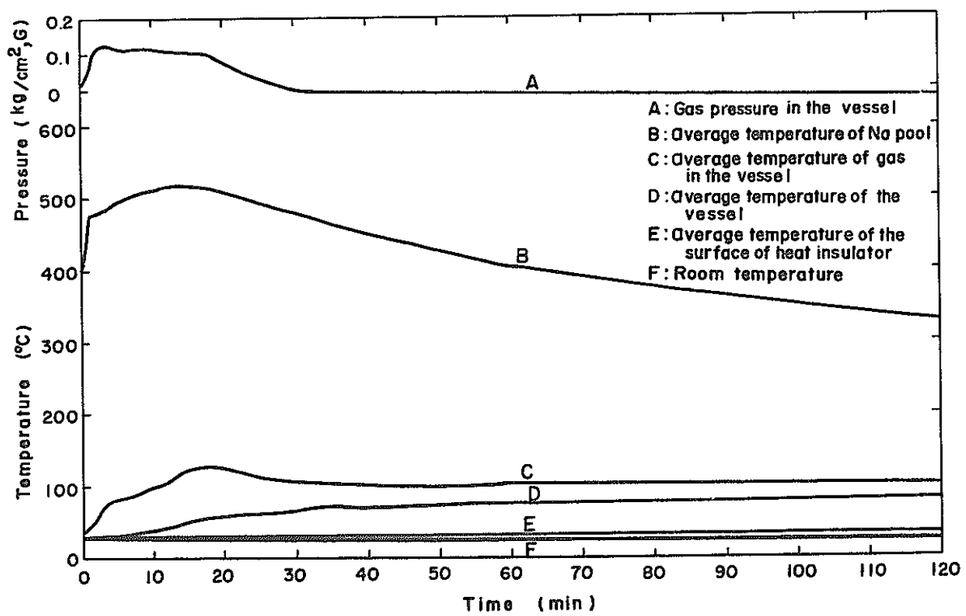


Fig. 5.5 Temperature and Pressure Response (Test No. 4)

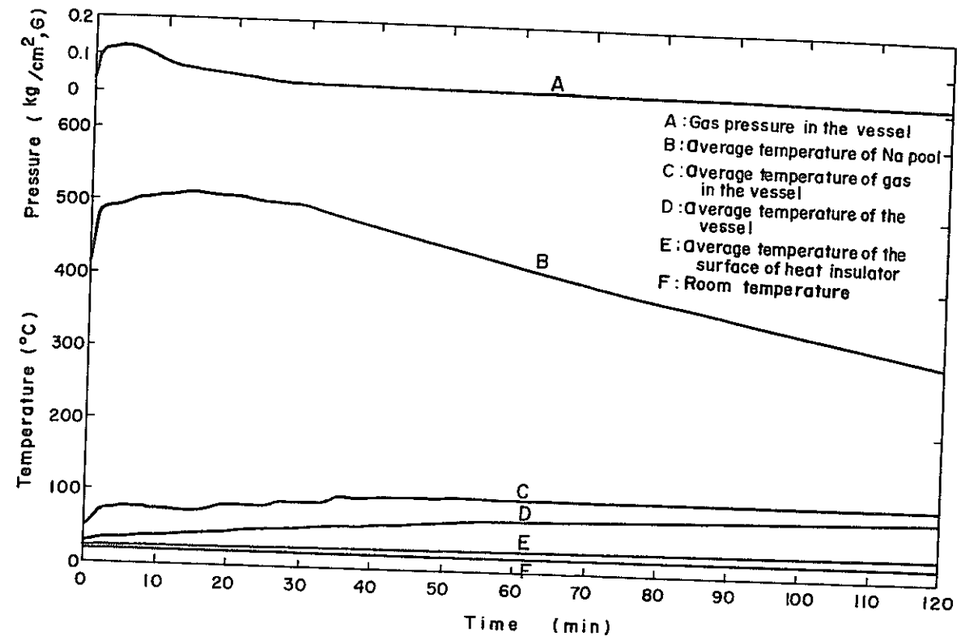


Fig. 5.6 Temperature and Pressure Response (Test No.5)

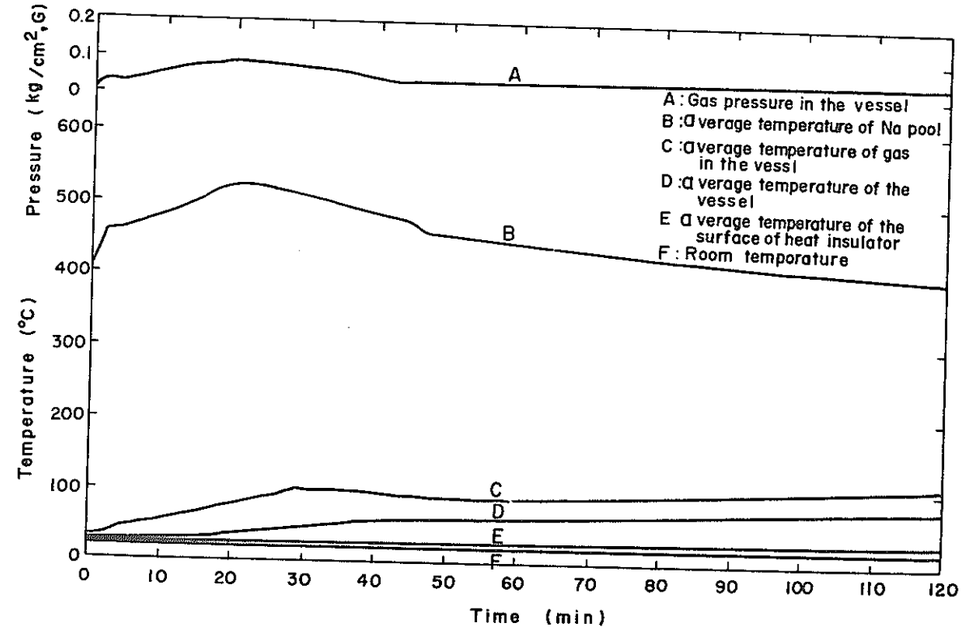


Fig. 5.7 Temperature and Pressure Response (Test No. 6)

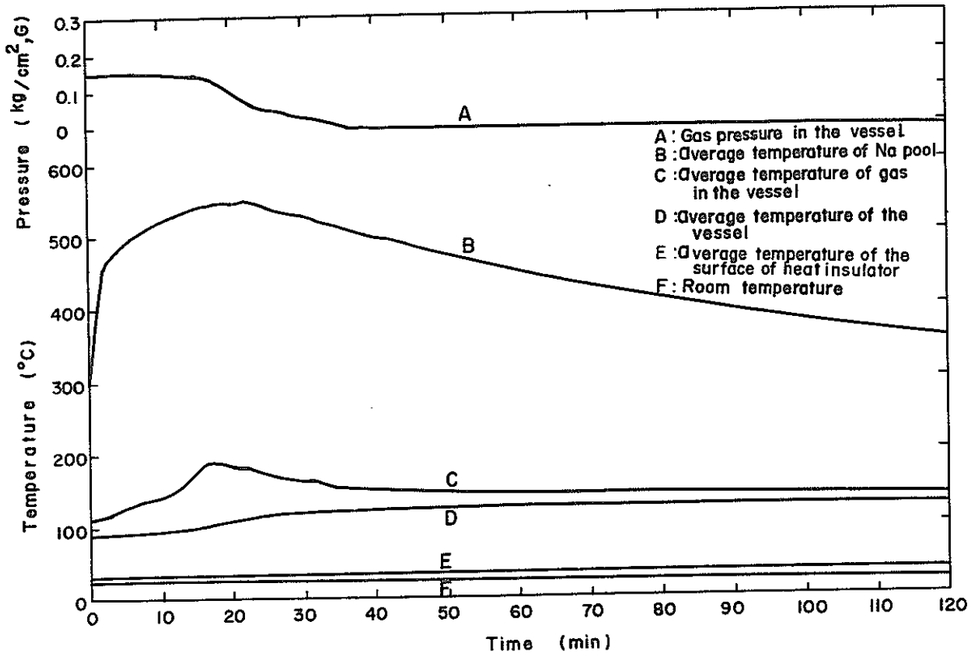


Fig. 5.8 Temperature and Pressure Response (Test No. 7)

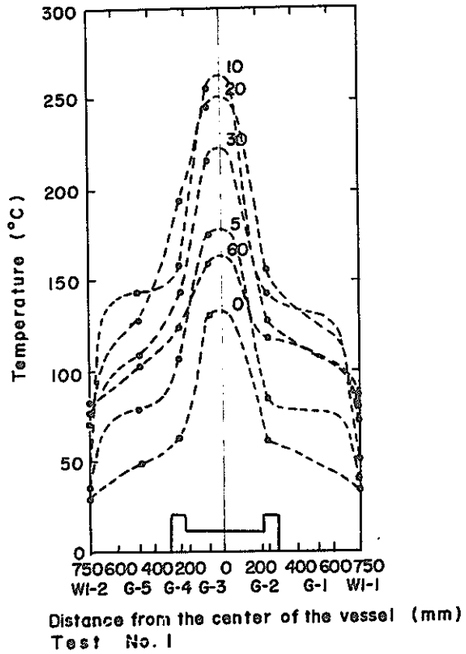


Fig. 5.9 Radial Distribution of Temperature in the Vessel

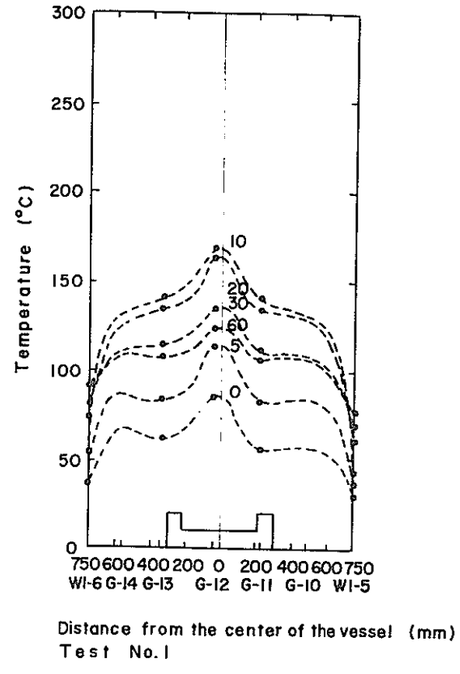


Fig. 5.10 Radial Distribution of Temperature in the Vessel

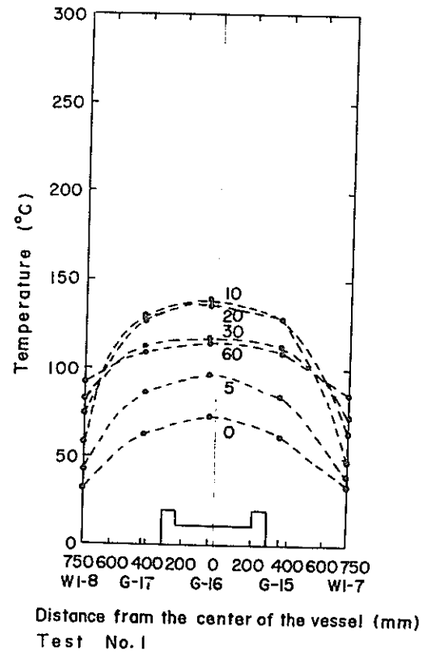


Fig. 5.11 Radial Distribution of Temperature in the Vessel

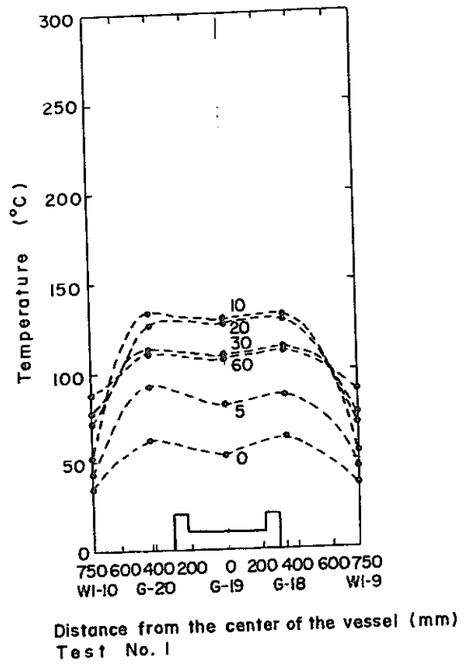


Fig. 5.12 Radial Distribution of Temperature in the Vessel

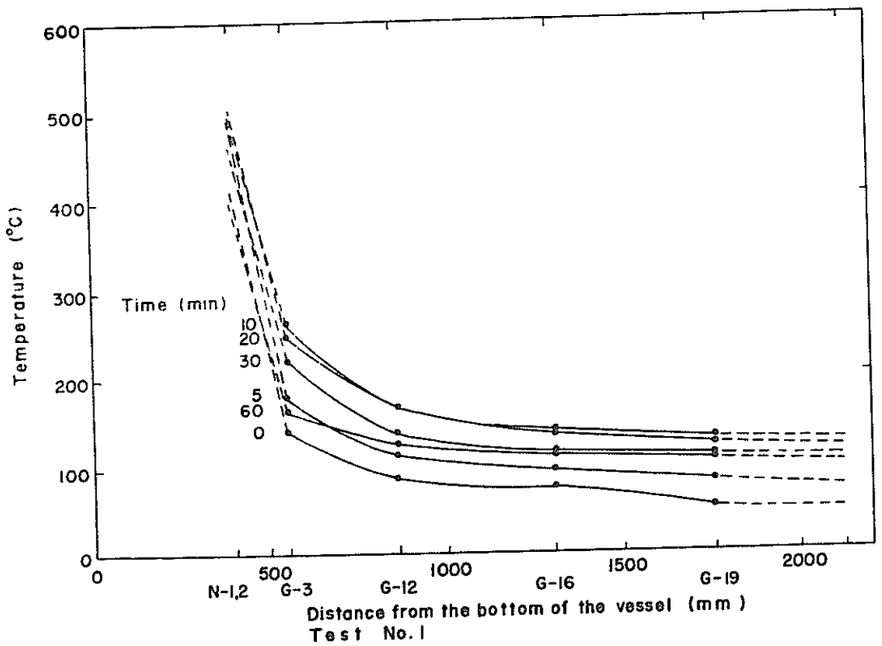


Fig. 5.13 Axial Distribution of Temperature

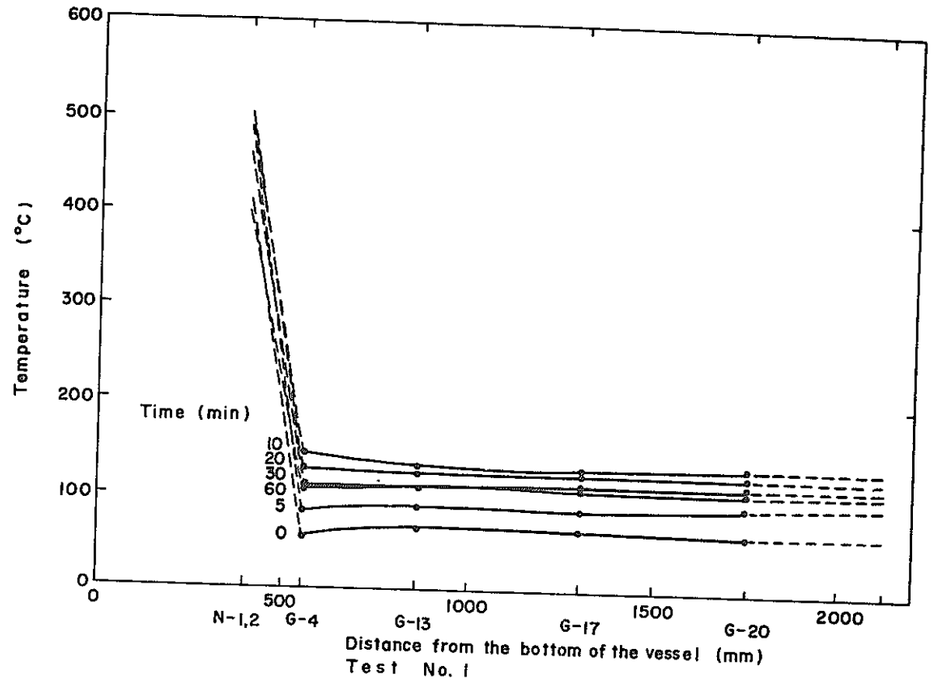


Fig. 5.14 Axial Distribution of Temperature

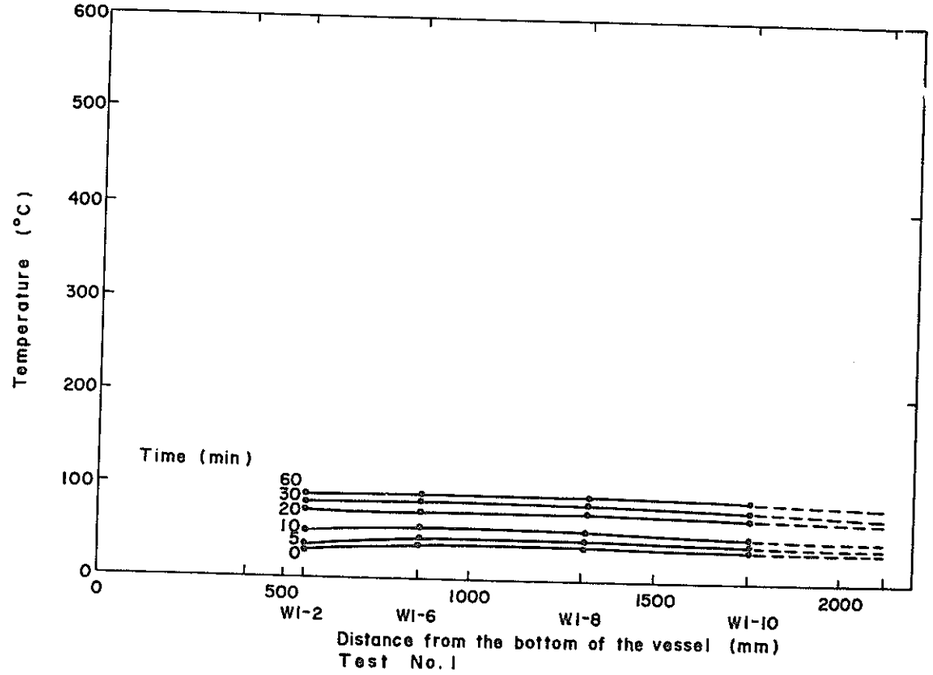


Fig. 5.15 Axial Distribution of Temperature

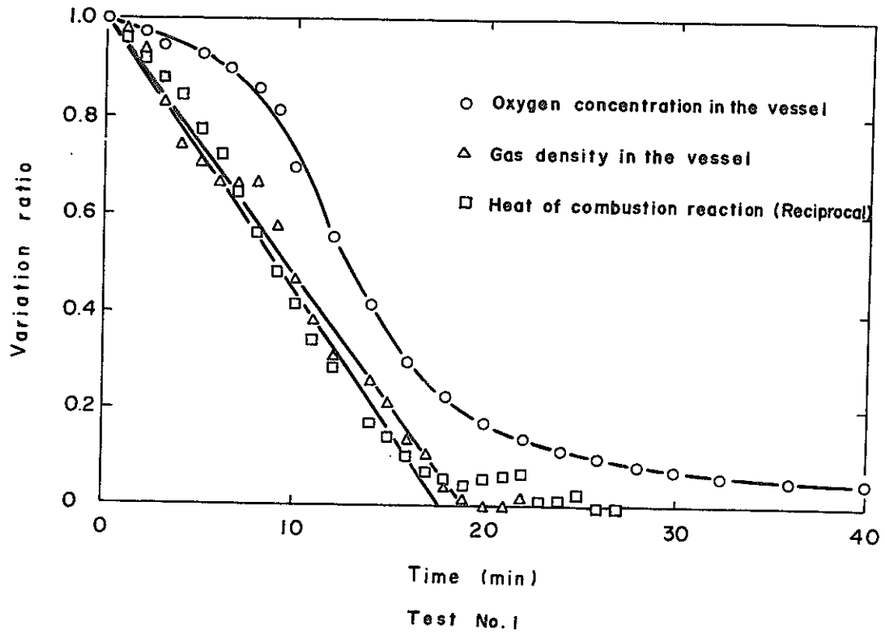


Fig. 5.16 Reaction Rate of Combustion and Oxygen Concentration in the Course of Time, in the Light of Thermodynamics

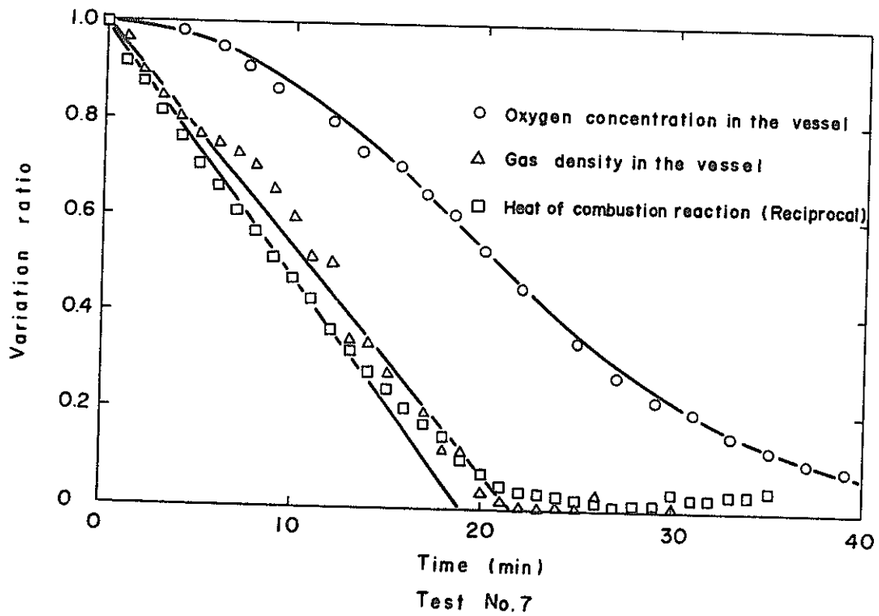


Fig. 5.17 Reaction Rate of Combustion and Oxygen Concentration in the Course of Time, in the Light of Thermodynamics

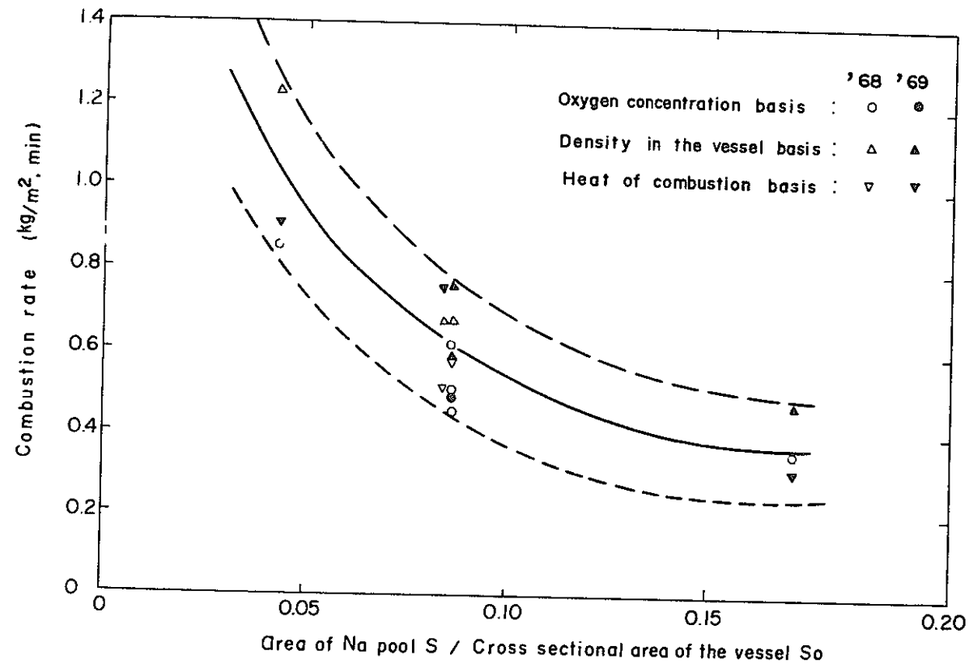


Fig. 6.1 Relationship between Area Ratio (S/So) and Combustion Rate