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IGNITION AND COMBUSTION OF SODIUM - FIRE CONSEQUENCES - EXTINGUISHMENT AND PREVENTION

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1 - INTRODUCTION

This document presents the results of work carried out at the IPSN on :

- sodium inflammation,
- sodium combustion (pool fires and sprayed jet fires),
- extinguishment (passive means and extinguishing powder)
- the physico-chemical behaviour of aerosols and their filtration,
- the protection means of concretes,
- intervention during and after a fire, treatment of residues, intervention equipment.

The calculation codes developed during these studies are described. The experimental basis which allowed the qualification of these codes and the technological means aimed at prevention and sodium fire fighting, was obtained using programmes carried out in the experimental facilities existing in Cadarache or in collaboration with the German teams of Karlsruhe.

2 - IGNITION OF METALS

2.1 - Theoretical aspects of ignition

Most of the time, studies undertaken to obtain precise information on the ignition temperature of metals did not yield concordant results. In fact, the ignition temperature may depend on a given number of factors such as the pureness of the metal considered, the moisture contents of the combustive gas used, pressure conditions, the dimensions of the test sample, the various treatments applied to the metal, the equipment and techniques of the process, the condition of the surface exposed to sodium, the oxidation rate of this surface etc...

The quality of the oxide layer built up on the surface is directly related to the ignition of metals. It might prevent the combustion reaction. In a general way, it may be stated that metal oxidation follows different laws in agreement with temperature variations ; these kinetic laws are responsible for the formation of superficial oxides which will cover the metal in various ways :

-at low temperatures, the kinetic law related to time is logarithmic : the oxide is a protective agent.

-at intermediate temperatures, the kinetic law is parabolic, the oxide layer is no longer a protective agent, but it prevents the direct action of oxygen which diffuses through this layer to react on the metal.

-at high temperatures, the oxygen consumption law is a linear function of time. The porosity of the oxide layer is sufficient to allow for oxidation.

These temperature ranges are particular to a metal. Burning is subjected to a metal temperature which is higher than the transition temperature from the parabolic range to the linear range. The value of this transition temperature moreover depends on different physical and chemical transformations liable to affect the metal-oxide.

- physical transformations : sublimation or fusion of the oxide, shrinkage due to phase changes, crackling of the layer due to differences in the thermal expansion coefficient of the metal and of its oxide.
- chemical processes : alterations of the chemical composition of the layer.

Given the transition temperature (parabolic oxidation range/linear oxidation range), ignition will take place if the quantity of heat produced by the oxidation reaction is higher than the loss of heat in the system. The fuel temperature is increased especially as the law of oxidation is generally an exponential function of temperature and this phenomenon will increase its speed continuously until combustion occurs.

2.2 - Sodium ignition

2.2.1 - Ignition in air

Experimental and theoretical figures taken from literature relating to the ignition temperature of sodium are given in TABLE 1 which also evidences the important differences from one value to another. Still some observations may be made on behalf of this situation :

- the figures for the ignition temperature obtained with a heated sodium pool are higher than those determined under the same operating conditions with an untroubled pool or with droplets. This is explained as follows : in the case of the heated pool, the metal temperature (sodium) is increased while it is not insulated from oxygen. During heating time, an oxide layer is formed at its surface which will inhibit combustion.

TABLE I

SODIUM IGNITION AND COMBUSTION

TABLE I Reference works	Ignition temperature in air (°C)			
	Droplets	Agitated pool	Untroubled pool	Heated pool
COWEN-VICKERS (experiments)	133 - 138		260	440-470
TOUZAIN			150	280
RICHARD	200			280
GRACIE-DROHER	120	204	288	
NEWMAN		150	320	
LONGTON			260	
GROSSE-CONWAY			118	
LEMARCHAND-JACOB			209	
MALET (experiments)			215	
MALET (theory)			200-201-224	
REYNOLDS (theory)			210	
I.P.S.N.		140		
Mrs. CASSELMAN			205	

- under the same operating conditions, the ignition temperature obtained for an agitated sodium pool is lower than the temperature obtained for an untroubled pool. In the same way, the ignition temperature of sodium in the form of droplets is lower than the same temperature obtained for an agitated pool.

In the first case (untroubled pool and agitated pool), the movement of the pool may entail fractures of the oxide layer. As for the case of droplets, it is known that the smaller the particle, the higher the pressure tension round it. Knowing that combustion is the consequence of a reaction of oxygen on sodium vapour, it is obvious that the ignition of a drop is easier when its diameter is smaller.

These consequences partly explain the differences among the figures shown in TABLE 1.

An experimental study carried out in a casing of 316 1 contents with an untroubled pool formed of 100 g of sodium evenly distributed over a surface of 113 cm ^{2} has evidenced that the ignition temperature of sodium in dry air is approximately 205 °C (TABLE II). The variation of this temperature in terms of the molar fraction of oxygen is not linear (Figure 1) . The minimum molar fraction of oxygen is not linear. The minimum molar fraction of oxygen which is the ignition threshold is equal to about 3%.

TABLE II

OXYGEN FRACTION	0.050	0.075	0.100	0.150	0.21
Ignition temperature (°C)	344	252	228	220	205

If these limit temperatures are not reached, the time necessary for the sodium to ignite is given by the law hereunder :

$$\log(\theta) = \frac{1}{T} \cdot e\left(A^{-2}x_{O_2} + B\right) - Cx_{O_2} + D$$

In which :

θ = ignition delay in seconds

T = initial temperature in K

x_{02}= molar fraction of oxygen.

This experimental law determines the ignition delay in a particular configuration and is certainly not effective for all systems. However, this phenomenon may have specific characteristics which correspond to an exponential form whose coefficients depend on experimental conditions.

2.2.3 - Detailed ignition process

Various tests have shown that ignition is always preceded by a formation of nodules on the surface of the metal. This nodule formation alone is not sufficient to start ignition. Observation of the metal surface by means of an I.R. camera has evidenced that the location of the nodules is directly related to over-temperature phenomena appearing on the surface of the metal. The following hypothesis has been made : the structure of the oxide film is heterogeneous (porosity, structure defects etc...) and this leads to uneven oxidation of the metal and to creation of preferential oxidation spots where temperature gradients are built up. This induces a system of tangential forces created by surface tension gradients (thermocapillary convection) leading to rupture of the oxide film and to formation of nodules. These nodules which are actually sodium droplets will become oxidised and their heating is faster than that of the remaining metal surface because of the high surface/ volume ratio. The thermal unbalance thus created will lead to ignition..

2.3 - Conclusion

It is important to note with respect to these considerations that finely divided sodium may be ignited even at room temperature. In such a case, the surface/volume ratio reaction is high thus allowing for quick temperature increase and entailing ignition.

For the personnel working with sodium, it is necessary to have available at a short distance the equipment required for firefighting and this regardless of the temperature at which the metal is handled.

When considering all these results, it is obvious that no attempt should be made to cool down the fire with a view to extinction.

3 - COMBUSTION

3.1-- Metal combustion

3.1.1 Different aspects of metal combustion

Metal combustion has only recently been the subject of research work, but is attracting increasing interest because of the development of spatial applications. Indeed, the advantage of the possible use of some metals as additives for propulsion resides in their high combustion temperature corresponding to a high transformation temperature and to fair stability of the reaction products.

After ignition, the combustion of a metal may continue on its surface or in a vapour phase. The characteristics of the second combustion mode are the presence of a luminous zone at a finite distance from the surface and the formation of oxide smoke composed of extremely fine particles. The simultaneous presence of liquid or solid oxide particles and of gaseous molecules or atoms (metal, actionless gas, oxygen) in the reactive zone gives heterogeneous features to metal combustion. Sometimes, the chemical processes are not well known as their study is complicated by the influence of diffusion and by other transfer processes which might act on the reaction and in this way mask the influence of kinetics as such. As a matter of fact, the chemical processes are most of the time the quickest stages of reaction because of the temperature attained in the flame.

GLASSMAN and then GLASSMAN and BRZUSTOWSKI inferred some general remarks from the thermodynamic and physical properties of metals and of their oxides :

- **temperature of the flame :** with a few exceptions, metal oxide molecules cannot exist in vapour condition and decompose rapidly into metal vapour and oxygen. This thermal instability of oxide particles therefore sets an upper limit to the flame temperature : the decomposition temperature of the oxide, generally considered as the boiling point.
- **the consequence** of this condition is the presence of condensed matter at high temperature in the reactive area.

- **the third remark** is related to the combustion process of a metal (vapour phase on surface combustion). The flame area must be at a temperature equal to or higher than the metal surface while remaining at a temperature lower than or equal to that of the oxide decomposition, i.e.

T metal -< T flame -< T oxide decomposition

This leads to the following conclusions :

- the combustion process in the vapour phase will occur if energy is transferred from the flame to the metal surface to supply the latter with latent heat for vaporisation. This means that the flame temperature is higher than the surface temperature. This temperature difference only exists for metals for which the oxide boiling-point is higher than the metal boiling-point.
- for metals, when the boiling temperature is higher than the temperature of oxide decomposition, combustion will occur on the metal surface.

3.1.2 - Comparison with hydrocarbon fires

Thermodynamics :

The reaction of metal combustion is a complete reaction while combustion of carbonaceous matters leads to the formation of many "by-products" accompanying carbon dioxide (CO_2) and water, i.e. the "final" components of combustion. These combustion "by products" are generated by exothermic reactions, but sometimes also by endothermic reactions. This means that in the case of metals all the energy of metal combustion is dissipated in the air, but that in the case of hydrocarbon fires, the energy dissipated in only a fractional part of the theoretical energy which would have been generated by the combustion, had the reaction been complete.

Combustion chemistry :

For organic matter, the flame is of diffusion type, unstuck from the surface during evaporation, and the combustion products are generated in a series of elementary processes called chain reaction. The types of matter existing in the flame are either gaseous molecules or ions, but also carbon particles, the percentage of which varies depending on the oxygen content of the mixture. In the case of metals for which the flame is of diffusion type (or vapour phase), the reaction products are solid or liquid particles. The process at the origin of their formation is a process of nuclide forming and of growth of the particles thus formed. While in the case of a hydrocarbon flame the emission spectrum is basically composed of bands (molecules) or rays (atoms) accompanied by a slight continuous background, the emission spectrum of a metal flame is composed of an intense background partly masking the emission spectrum of intermediate elements.

Flame structure

While the temperature reached in the flame essentially depends on fuel and combustive matter, the main difference between a hydrocarbon flame and a metal flame resides in the temperature curve as shown in Figure 3.

While for metal fire the metal oxide particles act as a screen (the gas temperature above the centre of the fire decreases rapidly), the burnt gases of hydrocarbon fires will keep their temperature quite a long time. Because of these conditions, gases of this type are liable to be one of the causes of fire propagation.

3.2 - Sodium combustion

The boiling temperature of sodium is 881 °C ; monoxide starts evaporation at 1350 °C, a value equal to the measured flame temperature. In compliance with the third general remark on metal combustion, the combustion of sodium should be of the vapour-phase type. Indeed, the following will give details on what the experiment has taught us when studying two types of fires which are liable to occur

- sodium pool fire
- sodium jet (or spray) fire.

3.2.1 Sodium pool fire

These fires may occur whenever the leakage of a pipe allows sodium to flow into a vessel while the jet is not broken. They are for this reason localised phenomena.

Basic research completed on small quantifies of sodium (some ten mg) has shown that according to oxygen pressure and concentration, but also according to temperature, sodium burns either in vapour-phase with formation of $Na_2 0$ in the flame area and transformation of monoxide into peroxide at the end of the flame area (light emitters are gaseous atomic sodium and liquid or solid aerosols) (superficial oxidation of sodium could occur in this case) or on the surface with formation of peroxide (the emitter is molecular gaseous sodium Na_2). This research work also evidenced the inhibiting role ensured by the surface crust during combustion.

Under fire conditions of this type which might be commonly found (gaseous mixture : air, temperature of Na between 200°C and 500 °C) only combustion in gaseous phase will occur.

While for metal fire, the metal oxide particles act as a screen (the gas temperature above the centre of the fire decreases rapidly), the burnt gases of hydrocarbon fires will keep their temperature quite a long time. Because of these conditions, gases of this type are liable to be one of the causes of fire propagation.

The studies completed by the IPSN (Cadarache) on sodium fires ranging from 20 kg to 5 tons (temperature of Na from 140 °C to 840 °C and area from 0,125 to 50 m^2) provided exhaustive knowledge on sodium fires of medium and large size.

3.2.1.1 - Effects of sodium temperatures, of combustion surfaces and of pool thickness on the combustion rate.

TABLE III shows the results of fires with various initial sodium temperatures and under conditions including oxygen concentration variations.

- it seems that the initial sodium temperature has only minor effects on the average combustion rate. This is certainly due to the fact that the pool temperature stabilises during combustion at a value varying between 570°C and 750°C. Boiling temperature is never reached even if the initial temperature is close to 840°C.

- the average combustion rate seems to diminish when the combustion surface is increased. This is certainly an effect of the convection movements which in the case of large fire surfaces hinder the diffusion of oxygen in the centre of the sodium pool. This phenomenon stands out more clearly when initial combustion rates are considered, which from 49 $kg.h^{-1}.m^{-2}$ for a surface of 0.125 m^2 decrease to 36 $kg.\ h^{-1}\ m^{-2}$ for a surface of 1 m^2 and to 27.6 $kg.h^{-1}.m^{-2}$ for a surface of 10 m^2.

These results were confirmed during tests conducted within the framework of the ESMERALDA programme, in particular during the ESM 1.2 test (surface of fire 50 m^2, 5 tons of metal)

The thickness of the sodium pool has no effect on the combustion rate. On the other hand, it is possible to foresee the mass of burnt sodium using the formula :

$$m_b = K.S.d$$

with

- K=527 $kg.\ m^{-3}$ for fires burning in a variable atmosphere. In atmospheres with constant oxygen concentration ($O_2 = 0.21$) and perfectly dry air, this value rises to 774 $kg.\ m^{-3}$
- S = surface in m^2
- d = thickness of the sodium pool, in m.

Beyond d = 26.5 cm, the burnt mass is practically only dependent on the surface of combustion.

As for the quantity of sodium burnt and found again in the aerosols, it is equal to 45% maximum of the burnt mass. The aerosols are composed of sodium peroxide. The remainder of the burnt sodium contained in the combustion vessel is essentially made up of monoxide with small amounts of peroxide. At the end of the fire, the percentage of sodium burnt in the form of peroxide amounts to 52% as an average value.

TABLE III

Experiment	Initial sodium θ °C	Enclosure m^3	Thickness cm	Surface m^2	Average combustion ζ $kg.h^{-1} . m^{-2}$	Oxide throw out ζ
Cassandre 3	550	400	5.1	1	24.5	0.31
Cassandre 4	550	400	10	1	26.9	0.365
Cassandre 5	550	400	14	1	26.2	0.385
Cassandre 6	550	400	28.6	1	23.8	0.40
Cassandre 7	550	400	18.3	2	19.6	0.46
Cassandre 8	550	400	9.2	4	17.7	0.43
Lucifer 1	250	400	17.5	2	17.1	0.45
Lucifer 4	140	400	18.5	2	18.5	0.372
Lucifer 5	840	400	20.4	2	17.9	0.427
Drac	200	400	12.8	10	17.7	0.163
EBCOS	550	22	9.9	0.125	38.4	0.24

3.2.1.2 - Effects of humidity

Tests completed in a room of 22 m^3 determine the effects of humidity on the combustion rate have shown that humidity inhibits combustion up to a relative humidity of 30% at 20°C. This inhibiting effect disappears progressively from a degree of relative humidity of 60% on, but the value of the average combustion rate is not equal to that found in a dry atmosphere (fig.2). This inhibition of combustion is due to the formation of a film of soda on the surface of the metal ; this formation of soda is not due to the reaction of sodium with water vapour (indeed, no production of hydrogen is detectable), but to the action of the latter on the oxides formed during combustion.

3.2.1.3. Details of the combustion process

The bulk of these results made it possible to determine the exact process of sodium combustion (Figure 4) :

The aerosols come from a reaction in the vapour-phase. Their chemical state is sodium peroxide which in the case of a fire in open air is converted, in a first stage, into soda and then into carbonate.

These tests made it possible on the one hand to confirm that the flame is only slightly separated from the liquid metal and on the other hand that it is possible to approach a fire if one is protected against the chemical aggressiveness of the aerosols.

A theoretical study has shown that the slowest phenomena in sodium combustion, i.e. those governing the combustion kinetics, are on the one hand the diffusion of oxygen through the flame area to react with liquid sodium and to build up the layer and on the other hand the transfer of sodium vapour to the flame area (evaporation-diffusion).

This means that the combustion process is a double line of phenomena as shown in the diagram of Figure 4. However, some questions have not yet been answered, for example those on flame structure and the laws on nuclide formation and aerosol growth, the aerosol emissivity of the sodium pool, the effects of convection movements due to the fire on the aerosol emissivity of the sodium pool and on the combustion kinetics.

3.2.2 Sodium jet and spray fire

Experimental studies were carried out at Cadarache in POLLUX (3.7 m^3), MERCURE (22 m^3) PLUTON (400 m^3) and JUPITER (3600 m^3). Experiments of the same type were conducted in collaboration with the German partners in the FEUNA facility (220 m3) located in Karlsruhe.

The influence of the direction of the jet (250 to 550°C), of the temperature (0,15 $Kg.s^{-1}$ à 230 $Kg.s^{-1}$), of the obstacle and of the insulation was studied during this experimental programme.

Among these parameters, the direction of the jet appeared as being that which is the most important when considering the thermo-dynamic consequences of the fire. The upward jets at a temperature of 550°C and with impact on an obstacle were therefore the most studied. Under these conditions, the study showed that combustion was limited by the diffusion of oxygen towards the jet. Consequently, when the sodium flowrate increases, combustion efficiency (mass of sodium burnt/mass of sodium ejected) reaches a limit value close to 10 %. This limit is reached even faster when the volume of the room is small.

Thus the breaking up of rooms into separate units is efficient in reducing the thermo-dynamic consequences of a sodium jet.

<u>3.3 - Consequences of a fire</u>

3.3.1 - Thermodynamic consequences on installations

Two cases are to be considered : sodium pool fires and sodium spray fires.

3.3.1.1 -Thermodynamic consequences of a sodium pool fire

A « sodium pool fire » computer code (PYROS 1) has been qualified on the basis of results obtained and is currently used by Novatome for SuperPhenix calculations. This computer code makes it possible to foresee at any time and for a given confinement the temperature variations (sodium, surrounding gases, confinement walls), but also the over-pressures which may be generated by a fire of a given mass and surface. The energetic power of the source is calculated by taking into account the double mechanism of sodium combustion (superficial combustion and vapour phase combustion). At low temperatures (less than 350°C), superficial combustion is predominant. At high temperatures, vapour phase combustion is the most important phenomenon. We then use the Garellis formula (19)

$$\tau = \tau_0 \frac{n}{n_0} \sqrt{\frac{T}{T_0}}$$

τ = rate of combustion at the moment t
τ_0 = initial rate of combustion
n = number of oxygen moles at the moment t
n_0 = initial number of oxygen moles
T = gas temperature at the moment t (K)
T_0 = initial gas temperature (K)

The percentage of sodium converted into sodium peroxide and sodium monoxide is also taken into account :

$$Na + O_2 \rightarrow Na\,_20_2 \qquad AH = -124\ Kcal.mol^{-1}$$

$$2\ Na + 1/2\ 0_2 \rightarrow Na_2\ 0 \qquad AH = -104\ Kcal.mol^{-1}$$

For safety reasons, To is taken equal to 40 $kg.h^{-1}.m^{-2}$ which is a value higher than those of the experiments and the quantity of sodium in the form of peroxide is equal to 40% of the burnt mass ; the remainder is monoxide.

The energy produced by the combustion reaction is transferred :
- to the ground by conduction through the sodium mass,
- to the air - aerosol system by convection and radiation,
- to the walls by transfer from the air - aerosol system ; radiation and convection, experience having evidenced that direct radiation from the flame to the walls is equal to zero.

When establishing the energy balance, it is thus possible to calculate step by step the temperature variations of sodium, air and walls with the coefficients for heat exchange obtained by experiments.

With the oxygen consumption known, the over-pressure in the confinement is calculated assuming perfect gases. The thermal consequences on a confinement are therefore calculated with a margin for safety, the basic values and the proportion of sodium in the form of peroxide being pessimistic values.

Thus, these calculations may be completed taking into account the type of confinement for the room in case of fire

- air tight and pressure resistant
- air tight and pressure resistant to a given value only, beyond which the gas and aerosol mixture is released into a ventilation duct or directly into the open air.
- ventilated (natural ventilation, forced ventilation : draught stopped, extraction maintained).

In each case it is possible, thanks to a formula giving the physical behaviour (granulometry and concentration) of the aerosols in the room, to compute the quantity of aerosols which will be ejected from the accident room.

3.3.1.2 -Thermodynamic consequences of a sodium spray fire

The study of sodium spray fires and the development of computer codes allowing to foresee the consequences of fires of this type on the confinement are difficult because they require knowledge of the diameter of the sodium droplets and this parameter is not easily obtained.

Two codes have been developed. These are FEUMIX and PULSAR.

FEUMIX 3 is the latest version of this point code which globally represents the jet and the thermal transfers of the jet to the gases and the walls.

PULSAR 2 is a two-dimensional code describing the sodium jet trajectory (or the droplet trajectory) in the facility. The impact of sodium on the walls and the floor is taken into account.

The openings onto the outside are also modelled in these two codes.

3.3.2 Chemical consequences on installations

A distinction will be made between the effects of sodium on building materials and the effects of combustion products.

3.3.2.1 Sodium - materials reaction

The electro-positive character of sodium entails, for this metal, a very high reactivity with respect to a great number of materials. Thus, sodium will attack silica and all silica materials, transforming them into silicates. Phosphatic products and especially phosphated concretes are reduced. In the latter case, it is important to note that the product thus formed may react to the humidity of air. The consequence of this reaction is a formation of phosphorated hydrogen PH_3, a highly toxic product. In a general way, it might be said that all materials embodying mineral components liable to be reduced are attacked by sodium.

However, the most important reaction of sodium on materials is what is called the sodium - concrete reaction. Its importance is double : on the one hand, it concerns the high quantities of concrete used in constructions and on the other hand, it can possibly cause major damage.

One of the constituents of concrete is water, which is found either in free form or bound with other materials. The thermal effects on concrete entail dehydration. This water reacts with sodium thus freeing hydrogen and if the mixture of hydrogen and oxygen reaches a concentration which is sufficient for detonation, the latter will cause the projection of sodium particles. In this way, the detonation due to the H_2-0_2 reaction is accompanied by sodium spray fire.

The purpose of a current basic study at Cadarache is to obtain a better understanding of the sodium - concrete reaction. The first tests tend to prove that the speed of hydrogen production depends on the thickness of the concrete and on sodium temperature.

At 550 °C and for minor concrete thickness, a non-negligible part of the water may discharge through the cold face. This fraction decreases when the thickness of the concrete increases. The concrete temperature may reach values close to 800 °C and analyses completed a posteriori show that the attack of the concrete by sodium is mainly due to alkaline fusion of certain components of the conglomerate. The speed of sodium penetrating into the concrete reaches about 2 $cm.h^{-1}$. The analysis of reaction products has shown that some of the concrete constituents may be transformed during the attack and that these products will create carbonaceous products such as acetylene, ethylene and methane, when reacting with water vapour in air.

At 200 °C, the production of hydrogen and the penetration of sodium into concrete are practically non-existent.

To prevent this reaction, it is necessary to protect the concrete and to insulate it with a metal sheet. This is how the floor of the SUPER - PHENIX reactor was protected. More analytical studies have aided the development, in collaboration with EDF and the Société des Ciments Lafarge, a concrete which is inert to sodium (BIS). This concrete can be applied as a protective layer over ordinary concrete. Tested on a tank of 10 m^2 with a leak of 1 ton of sodium at 550°C, this protection revealed itself to be very efficient. It was not attacked and the concrete placed under the BIS layer remained intact.

3.3.2.2 - Desorption of water from concrete

The R and D studies in this area have allowed to develop the SORBET calculation code. This code describes the migration of water in a concrete subjected to a thermal stress. This migration occurs towards the cold face and towards the hot face of the concrete. The thermal decomposition of carbonates is also taken into account. Experiments conducted on concrete blocks of 1 m^3 (surface 1 m^2 sodium temperature 800°C) were used to establish the qualification book of SORBET.

3.3.2.3- Reaction of combustion residues on materials

Because of the extremely corrosive nature of soda, we shall insist in this paragraph on the highly oxidising power of sodium aerosols. Various experiments have shown that the aerosols are sodium peroxide. This compound is highly hygroscopic and changes into soda as follows ;

$$Na_20_2 + H_20- \rightarrow 2\ NaOH + 1/2\ 0_2 \quad 26\ kcal.mol^{-1} \quad (1)$$

Actually, this reaction passes through the formation of hydrogen peroxide ($H_2 0_2$) which in turn is decomposed under a double influence of thermal (reaction heat) and chemical (presence of soda) nature. This decomposition is liable to produce nascent oxygen which is particularly reactive. This is what made it possible to explain the phenomenon of secondary combustion noticed when the room was again submitted to the ambient atmosphere prior to the arrival of the personnel. The organic elements in the room and especially paint are liable to burn. This phenomenon appears when the oxide deposit contains more than 500 $g.m^{-2}$ of sodium. It is therefore advisable, during an intervention following a sodium fire in a room, to take all possible precautions in particular when the quantity of aerosols produced is large. The suddenness with which the phenomenon occurs is liable to endanger the life of the intervening personnel.

3.3.3 Consequences on the environment

The sodium combustion reaction produces two forms of residues : the aerosols and the crust (or layer).

Initially the aerosols are composed of sodium peroxide which in open air could be transformed at first into hydroxide and then into carbonate.

The crust is a mixture of sodium, monoxide and peroxide which may also evolve into soda and carbonate. These highly reactive products, especially peroxide and soda, are harmful to men, but also to the environment.

3.3.3.1 - Effects on the human body

The caustic effects of soda are well known. The lethal dose for the human body is 20 g ; the skin can withstand a 1% solution. The tolerance specifications for the PH of water are 8.5 in France. For the workers, the Institut National de Recherche et de Sécurité (National Institute for Research and Safety) takes into consideration the following concentration limits in the atmosphere :

USA	2 $mg.m^{-3}$	
Russia	0.5 $mg.m^{-3}$	
Great-Britain		
	2 $mg.m^{-3}$	continuous exposure
	50 $mg.m^{-3}$	(tolerable visibility 15 m)
	100 $mg.m^{-3}$	uncomfortable feeling for the eyes and the lungs. Loss of visibility.
	200 $mg.m^{-3}$	visibility equal to zero.

England has completed these specifications for the limit values under continuous exposure

2 $mg.m^{-3}$	hydroxide

0.2 $mg.m^{-3}$	oxide	continuous exposure
10 $mg.m^{-3}$	carbonate	

3.3.3.2 - Effects on the environment

The effects of compounds containing soda on the environment are either short-term or long-term - Short-term effects. These damages result for the flora in burns and perforations of the leaf surface due to the exothermic transformation reactions and to hydration of the initial oxygen. It is possible that the harmful effects of carbonate and bicarbonate aerosols are somewhat less severe, but there are no data available on this subject. Experiments have been carried out in France with sodium oxide aerosols and have demonstrated that damage of this nature is short-lived.

The experimental studies on the atmospheric dispersion of aerosols conducted using tests in open air (DIFNA experiment) or using the SATURNE tower (2000 m^3) within the framework of the ESMERALDA programme have shown that the chemical transformation of peroxide into soda then carbonate is extremely fast, the chemical analysis methods being too slow compared to the speed of the chemical reaction. These tests have nevertheless enabled us to determine the speeds of deposit on the ground, values which were introduced in an atmospheric dispersion code, ICAIRNA, a puff model which describes the atmospheric dispersion of aerosols .

- Long-term effects

Rain and running water pick up the sodium deposited in the soil. The effects of Na^+ ions are made conspicuous in two ways ; on plants they will entail variations of the osmotic pressure between the plant cell and the soil solution ; on soils they will cause an exchange of Ca^{++} and Mg^{++} ions thus entailing alkalisation and the beginning of processes leading to damage for the soil.

The effects are proportional to concentration and have no threshold. This means that damage to leaves starts when the rate of Na + in the soil solution reaches 0.05 % and the danger of soil alkalisation is very high for a S.A.R. (Sodium Adsorption Ratio) of 2.25. Aspersion is the most destructive way of attack. Thus aspersion by means of a 2 $g.l^{-1}$ solution will cause the yield to drop by 30%. As an example, approximate calculations show that such a concentration is equal to a rain of 10 $mm.h^{-1}$ for an hour occurring after a deposit of 20 $g.m^{-2}$ of sodium equivalent.

4 - INTERVENTION DURING AND AFTER A FIRE. PLANT REPAIR AND RESIDUE PROCESSING

Thanks to these large and small scale experimental programmes, rules of conduct have been adopted concerning :

- intervention during a fire ; for example, in order to avoid too great a production of aerosols which would lead to an early repair of the filters and re-inflammation risks of organic matters (see paragraph 3.3.2.3), it is recommended to not ventilate the room during the fire, only the opening must remain open ;

- the intervention after a fire and the repair of the room ; these rules concern the precautions to be taken before the intervention of personnel in the damaged room, the cleaning procedures, the intervention clothing and the tools used to retrieve the sodium ;
- the treatment of combustion residues, their storage and their transformation into soda.

These methods were validated during the large scale tests within the framework of the ESMERALDA programme.

They were also described in detail during the fourth international conference on liquid metal technology (LIMET'88- 17/21 October 1988 in Avignon page 203)

5 - FILTRATION AND PREFILTRATION OF SODIUM AEROSOLS

In order to avoid the release of aerosols outside the room, the ventilation system should comprise filters and prefilters.

Pre-filtration of sodium aerosols is required because of the very small quantifies of aerosols retained by highly efficient filter cells as shown in TABLE IV.

TABLE IV

Filter	Surface m^2	Test flow m^3/h	Retaining power g Na
SOLFILTRA	45	1 500	270
ASTROCEL I (AAF)	21.4	1.500	126
ASTROCEL II (AAF)	34.5	1.500	177

Pre-filtration tests carried out in a ventilation loop of 1500 $m^3.h^{-1}$, installed adjacent to the experimental tank of 400 m^3, have shown that no equipment normally available on the market is in compliance with the specifications required. For this reason, the IPSN has undertaken to improve two water pre-filters. One of them is the Colag filter whose improvements made it possible to increase the initial percentage of efficiency from 84% obtained with the equipment shown in Diagram 1 (Figure 5) to 99.2%. The other filter is the Aqualine R (initial equipment Diagram 2, Figure 5) whose efficiency was increased from 70% to 99.9%.

These results have been obtained with draining of the washing water in the pre-filters. Additional tests have shown that the operation of the equipment in a closed water loop (concentration of soda increasing as the aerosols are trapped) will not alter the efficiency or the devices developed.

6 - FIRE EXTINCTION AND MEANS

The study of ignition has evidenced that there is a risk of ignition and of burning of the metal below 114°C. Actually, this metal may cause fire even at room temperature when it is finely divided : attempts to lower the temperature of the metal during sodium fire fighting will be useless.

The phenomena which are predominant in combustion are oxygen diffusion and sodium vapour transfer. Fighting these fires therefore means trying to insulate the combustive material from the fuel. Keeping these facts in mind, studies have been undertaken in order to develop smothering systems whose purpose is to limit the consequences of a pool fire and extinguishing powders which should provide additional help to such devices.

6.1 - Passive means

6.1.1- Smothering tanks

The tests on smothering tanks carried out in the PLUTON facility (400 m^3) have led to the development of a device with which the following results have been obtained :

- for one ton of Na poured into the tank, only 30 kg burnt.
- the combustion speed is reduced by a factor of 10.
- the temperature of the sodium in the tank decreased immediately.

Later on, further tests made it possible to examine the connection between the tanks so as to increase the retention capacity of the system and to cover the whole surface concerned by a possible leakage. The result obtained by the connection of four tanks marks another progress : for a ton of Na poured into the tank, only 12 kg were burnt. This system operates according to the following principle (Figures 6) the sodium drops onto the smothering tanks and flows down the slopes of the V-shaped plates. The metal consequently flows downwards to the lowest point where hinged flaps are provided. Actuated by the sodium weight, the hinged flaps open and the metal flows down to the bottom of the tank. When the leakage is stopped, the hinged flaps take up their initial position again. This system formed of inclined planes and hinged flaps will thus insulate the metal from the oxygen.

The scale effects (in particular the thermal stresses between tanks) have been verified during the ESMERALDA tests thus qualifying the facility in case of large sodium leaks.

6.1.2 - GRAPHEX CK 23

This graphite compound which contains sulphuric acid can expand when exposed to thermal shocks. It is currently under examination at the C.E.A. Its interest is that it may be stored under certain circuits where it is not possible to install smothering tanks. However, this requires a research programme in order to determine :

- the efficiency of the product in relation to temperatures (in fact, its expansion will only start at 250°C and the expansion power depends on temperature).
- the quantity of the product required to extinguish fire.

-The behaviour of sulphuric acid.

- the problem related to the use of this product after the fire. In fact, the expanded product constitutes, for the sodium, a very large surface of pores into which the metal penetrates. This means that the sodium is then in a state of division which will facilitate its ignition at room temperature when the facilities are repaired.

6.1.3 - Funnelling floors

The idea of this technique is to give the ground a sufficient slope to bring the sodium to a low point in the room from which a duct will evacuate it into a recovery tank. This technique allows to evacuate the sodium from the damaged room towards the tanks

The slope (3%), the thermal effects due to the transfer of sodium in incompletely filled channels, the efficiency of such facilities have been qualified during specific tests performed in the SATURNE tower (2000 m^3) within the framework of the ESMERALDA programme.

6.2 Active means - Powders

Until 1975, studies achieved in the IPSN. had shown that the only efficient extinguishing agent was the Totalit MI powder. As a matter of fact, perlite and vermiculite, because of their high content of bound silica, react violently with sodium ; sodium carbonate and ANSUL Nax are poor extinguishing agents. The Totalit MI however has the disadvantage of being a sodium chloride compound embedded in organic materials which also contain CN bonds in their formula. The sodium chloride drags the important corrosion products into the ducts and the organic materials react with the sodium, discharging cyanides into the air.

Moreover, tests conducted at the IPSN following the TRENTE (Italy) accident during which 30 tons of sodium had been "extinguished" with cement, have shown that this product must absolutely be avoided with sodium fires. Its application induces violent chemical reactions which very rapidly increase the temperature of the mixture to a value close to 800°C. These reactions lead to the formation of carbide which, with the humidity of air, decomposes into acetylene.

For this reason, the IPSN. assisted by the C.N.R.S. has undertaken a study to develop a powder mainly composed of alkaline carbonate and graphite (Marcalina) which is about five times more efficient than Totalit. The advantage of this powder for the operator is that it can adhere to vertical and horizontal walls. In addition, it is also efficient against hydrocarbon fires. The studies concerning the Marcalina powder were aimed at storage and the application of this product in portable, moving and stationary equipment. Devices with various capacities have been designed (9 l, 20 l, 40 l, 70 l, 150 l, 320 l,1000 l and more). The physical and mechanical characteristics of this powder in its tanks are by now well known. This type of equipment is currently used in C.E.A. centres where sodium is used. The experimental tank of 400 m3 has been used for studies on a fixed installation comprising powder tanks (1/3 scale of Super-Phenix) and pipes (the length of which is equal to those of Super-Phenix). This installation is operative with material outputs and concentrations (material / carrier gas) which are those retained for SuperPhenix.

The efficiency of the transportation and powder spreading as well as the powder itself was verified during tests performed in the JUPITER vessel (3600 m^3), tests using 20 tons of metal sodium.

7 - PROTECTIVE CLOTHING

The preceding chapters of this document have already given detailed information on certain points concerning possible prevention ; preventive action has also been suggested to avoid fire breaking out or to limit its consequences. Nevertheless, it is necessary for the personnel working near sodium to be protected against aggression by this metal and thus to wear adequate clothing.

Tests have indeed demonstrated that a sodium leakage at 200 °C will set fire to the whole outfit if it is made of cotton or of Kermel. Also, many tests carried out on synthetic fabric have shown that Nomex alone resists sodium at 250°C. Beyond this temperature, the fabric is locally damaged, but it will not catch fire. The exploitation personnel of the C.E.A. is therefore wearing the ETNA 100 clothing which is mainly made of Nomex. This outfit is completed by rubber boots as it has been discovered that this material resists better to sodium than leather (the latter gets hard when heated) and by a polyurethane helmet.

The agent who will have to fight a sodium fire wears a PARNA outfit which also protects the individual gas cylinder on his back.

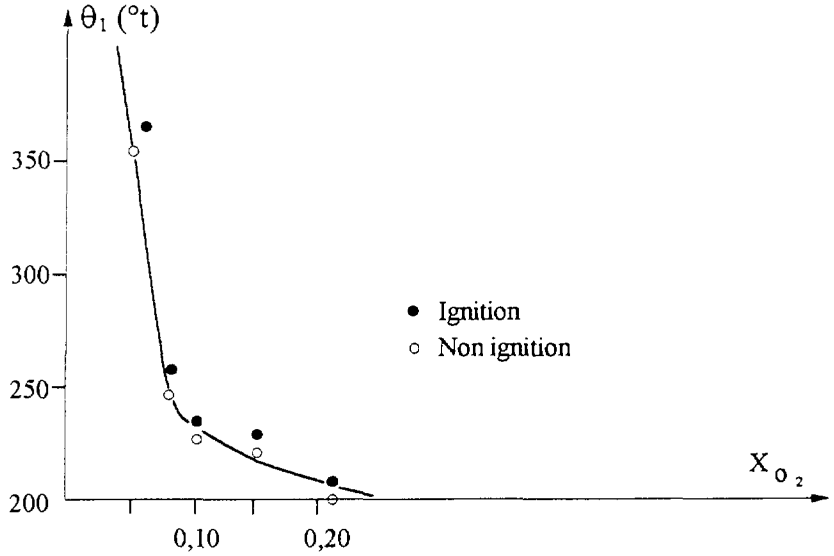
8 - CONCLUSION

The studies achieved by the IPSN since 1972 have led to a good knowledge of sodium fires and of the problems related to them. These studies have allowed us to acquire a very extensive knowledge on all the aspects of sodium fires, to develop codes, tools, means of fighting and preventing these fires. The scale effects have been properly understood with tests of pool fires of 50 m^2 in surface, sodium jets at a flowrate of 230 $kg.s^{-1}$, with a jet speed of 10 $m.s^{-1}$ maintained during 10 seconds and extinguishment tests using 20 tons of sodium.

9 - Remarks

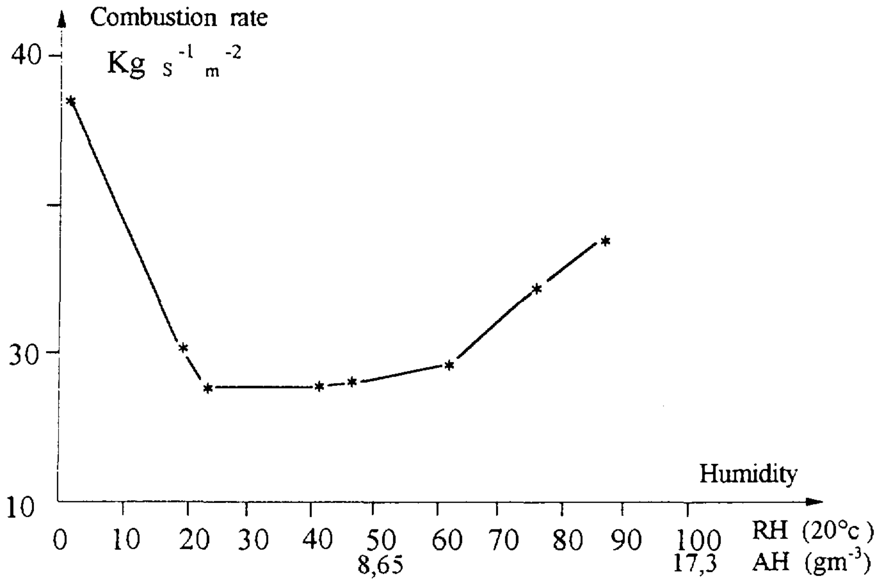
9.1 - This data base on sodium fires could not have been created without the participation and the competence of Mrs. CASSELMAN and RIGOLLET, Mr. J. CERCY, J. COLOME, J. CHARPENEL, G. DUVERGER de CUY, W. LESAUX, G. MIACHON, R. RZEKIECKI,. These engineers or PhDs in physics ensured, at the Laboratoire d'Expérimentation et de Modélisation des Feux of the IPSN, the role of test conductor and developed then qualified the calculation programmes mentioned in this document. The calculation codes (numerical and computer) were developed with the help of Ms MALAMAS , an engineer at the CISI, a computer firm specialised in the development of scientific programmes. Also, these tests could not have been conducted without the professionalism of all the technicians. During all these years, there has been no serious accident of any personnel due to a very reactive chemical product. Finally, this work could not have been carried out without the requests of "clients" whether they be Safety (IPSN) of Project (EDF, NOVATOME).

9.2 - The information provided in this document has all been published during seminars or international meetings. The list of publications is available at the Laboratoire d'Expérimentation et de Modélisation des Feux as it is too long to be given in the references of this document.



INFLAMMABILITY LIMITS

Figure 1



Mean Combustion Rate Versus Humidity

Figure 2

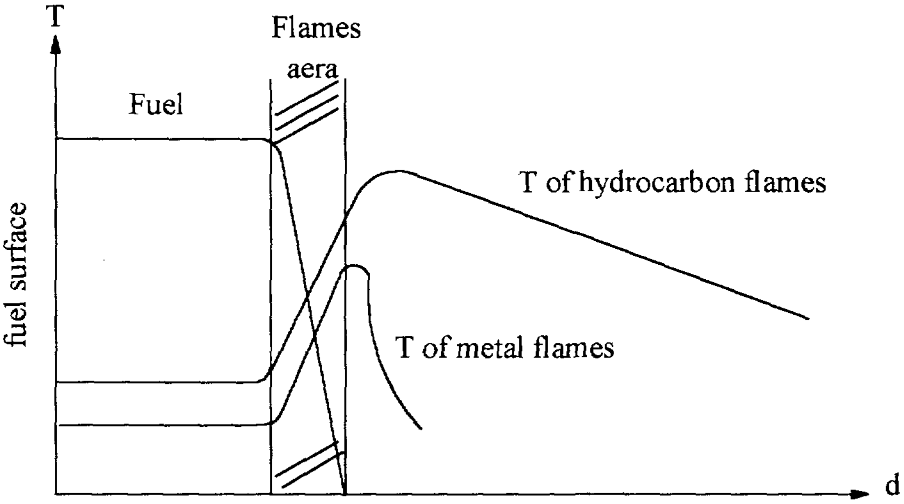

T
Flames
aera
Fuel
fuel surface
T of hydrocarbon flames
T of metal flames
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Figure 3

The double process of

COMBUSTION OF SODIUM POOLS

(vapour-phase and liquid phase)

FIGURE 3

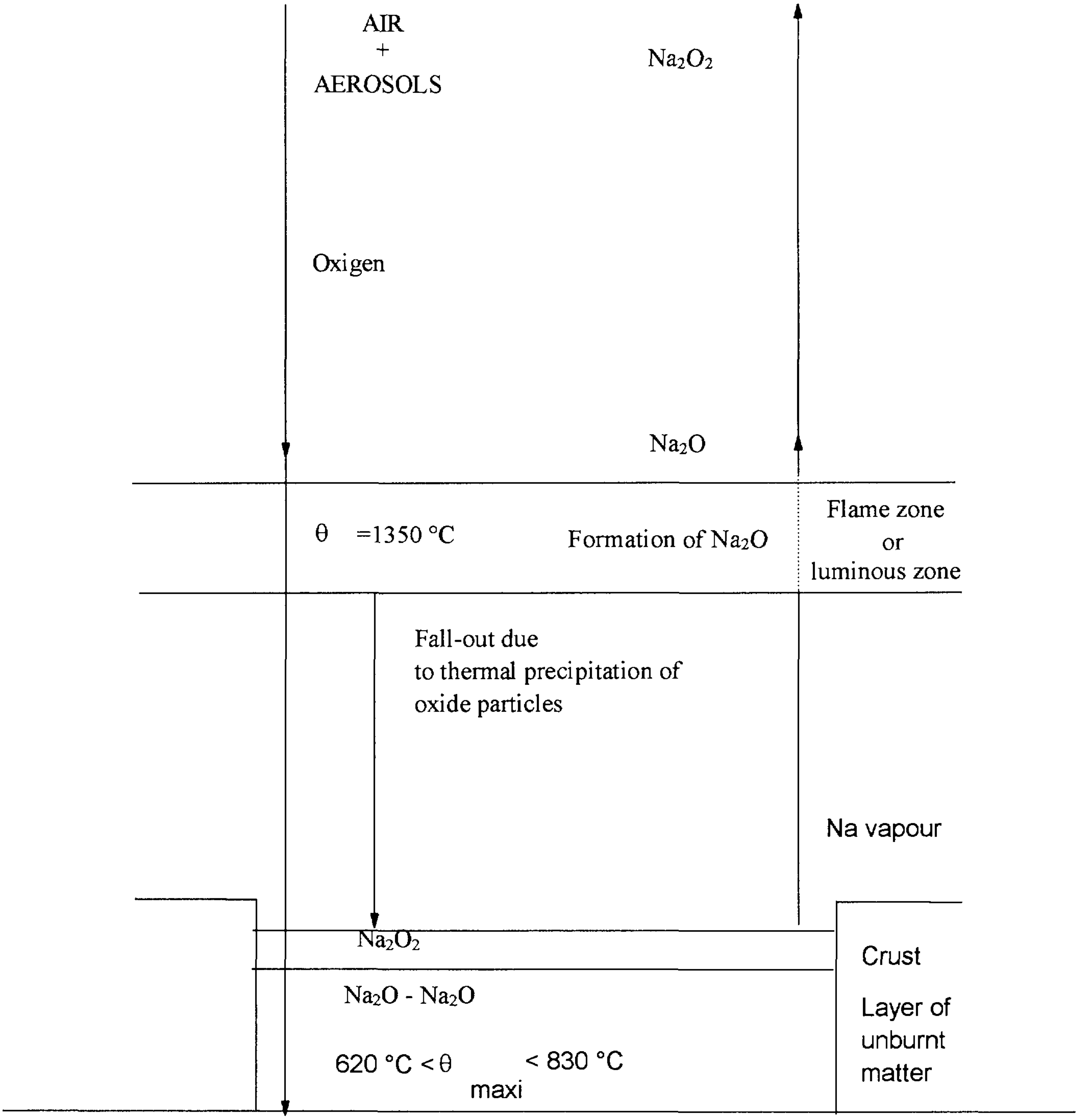
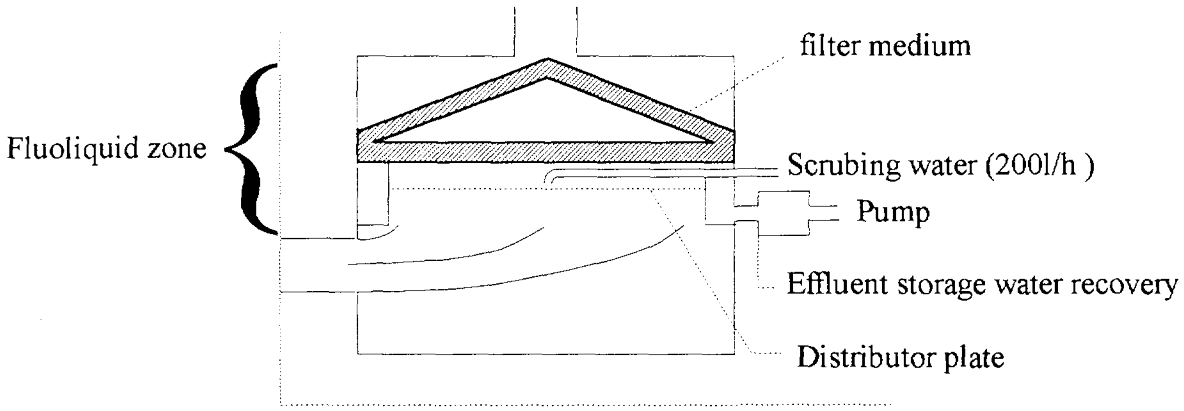


Figure 4

COLAG (A.A.F.)



AQUALINE R (NEU)

OPERATING DIAGRAM

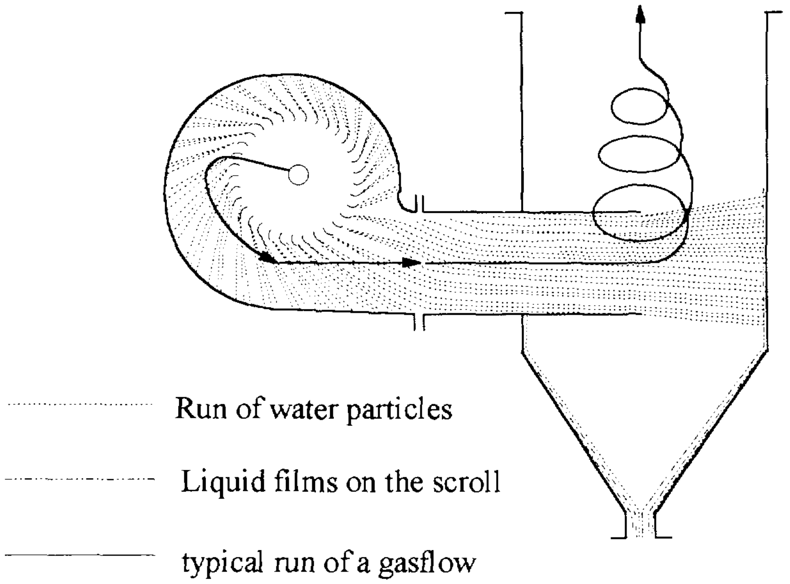
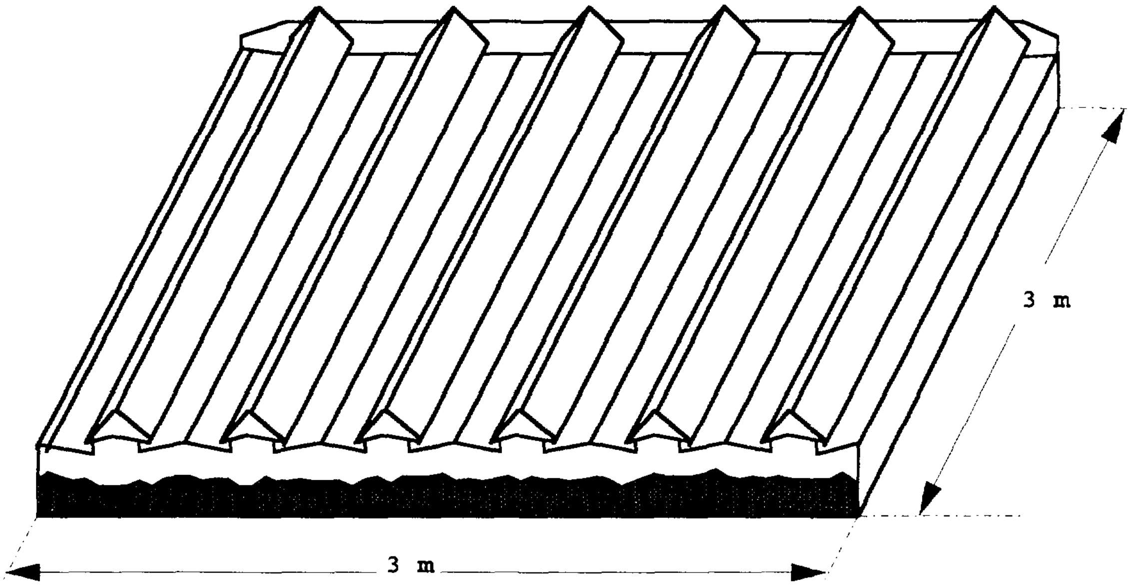
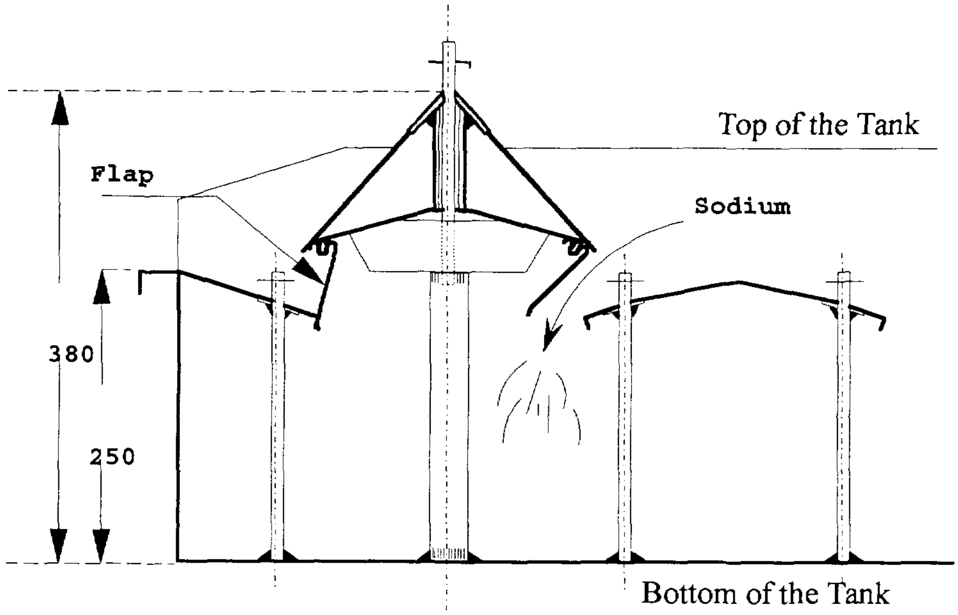


Figure 5



Smothering Tank (element unit)



Smothering Tank (assembly details of various parts)

Figure 6

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