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Analysis of the fire hazards on bituminization in nuclear fuel reprocessing

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1.Introduction

1.1. General introduction

The importance of nuclear safety has clearly been recognized and the accidents should be prevented. The nuclear fuel cycle facilities have a potential hazard, where the fissile materials are treated under reduction and oxidation process using organic solvents, which is not potentially safe either. A report [1] on the incidents in nuclear fuel recycle facilities has published. The significant incidents are mainly classified as follows:

- Criticality
- Fire and Explosion
- Release of radioactive materials or/and contamination

Such incidents could also provide valuable information. Table 1.1 gives incidents in different kinds of facilities. It shows that most of the incidents were reported at reprocessing and chemical processing plants. Especially the fire and explosion accidents often have occurred in reprocessing plants. Once the fire and explosion accident happened, some contamination and leakage of radioactivity usually occurred. In recent three years (1997-2000) in Japan, the fire and explosion accident in PNC Tokai Works and the criticality accident at JCO Tokai Uranium processing plant occurred. Research activities to prevent such accidents are very important.

On March 11 in 1997, there occurred a fire and explosion incident at the Tokai Bituminization Facility. After the accident, an investigation committee was organized and a lot of investigation and research works have been performed. A scenario to the accident was assumed by the investigation committee [2], but unfortunately the cause of the accident could not be completely specified. The analysis is very difficult because a lot of events are related.

The bituminized product is mixture of organic materials and metal nitrates. The reaction in the bituminized product may occur in the same as the red-oil reaction in the PUREX process. We should comprehensively report that the red-oil accidents occurred in the PUREX facilities over the world before the commercially based nuclear reprocessing plant using PUREX process is to start up on 2005 at the Japan Nuclear Fuel Limited (JNFL) Rokkasho village facilities in Japan (<http://www.jnfl.co.jp/>). The red-oil and bituminized product leads to an easily explosive hazard resulting from the mixture of organic materials and nitric acid in addition to its self-radioactivity. In the radioactive waste (LLW) treatment facilities and PUREX reprocessing plants, special chemical agents to immobilize ^{90}Sr , $^{137,139}\text{Cs}$ and ^{129}I were added; we should take it into account that these chemical agents may be concerned with the accident.

From the viewpoint of safety & control (S&C), it is very important to analyze and discuss the past accidents. Why does the accident occur? Where is the potential hazard in the process? We cannot help using a lot of organic solvents and nitric acid in the PUREX reprocessing plant. The potential risk seems to be so high. Nogami *et al.* [3] reported a new nuclear fuel reprocessing system based on pyridine type ion exchange process and Asano *et al.* [4] reported new nuclear fuel reprocessing system based on mild aqueous solutions. However, their methods are not commercialized. Moreover, in Japan, the plant technique is

imported from foreign countries; even the researchers and technicians are short of the technical knowledge, and they seem not to be very familiar to where the hazardous point is.

1.2. The purpose of the present study

In Chapter 2, we will show the general trend of accident analysis of Tokai Bituminization Demonstration Facility (BDF). The cause of the accident could not be completely determined. Historically, fire and explosion accident in nuclear facilities relating to the PUREX process was classified as follows:

- (a) Organic compounds (TBP, EDTA) + Inorganic compounds (nitrate salts)

TOMSK-7, SRP and Bituminization Facility in Tokai Works

- (b) Inorganic compounds (nitrate salts)

Chelyabinsk-65 and Hanford

These accidents were discussed in detail in the next section. Ignition temperature shows about 200°C in the waste type (a). On the other side, ignition temperature is about 350°C in the waste type (b). The waste which contains organic compounds more readily causes a run-away reaction than the waste which does not. There is no research work about the accident of Tokai bituminization process from the viewpoint of the chemical reaction between organic compounds and nitrates. The aim of this work is not necessarily to specify the cause of the accident in Tokai Bituminization Demonstration Facility, but to clarify hazardous chemical reactions relating to the bituminization process.

1.3. Construction of the present thesis

This thesis is separated into seven chapters. It is pointed out that the background and the necessity of this work in chapter 1.

Chapter 2 reviews the accident reports of Savannah River Plant, Chelyabinsk-65, Hanford, Toms-7 and Tokai Bituminization Facility for the viewpoint of runaway reactions of nitrates. From these incidents information of general hazardous chemical reactions in nuclear facilities can be obtained.

Chapter 3 shows the experimental apparatus and schemes of analyses. There are general thermal analyses such as DSC, TG-DTA, ARC and DIERS. Thermal evaluation of bitumen and nitrates was conducted by the simple TG-DTA. We have confirmed that the single bitumen and nitrates have not so much potential hazard. The evaluation apparatus of reaction of bitumen / nitrate mixture is a hand-made type furnace and temperature measurement system. From the viewpoint of chemical hazardous reaction between organic compound and nitrates, some amount of the sample is needed for experimental analysis. In a large amount of test, there are dangers for fire and explosion. After try and error experiments, sustainable data can be obtained by the hand-made experimental apparatus.

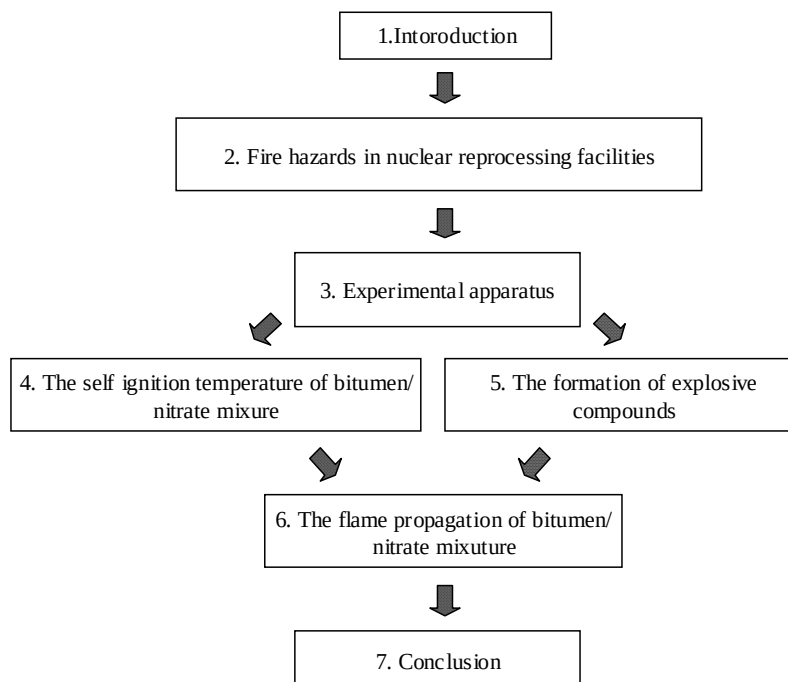
Chapter 4 views the result of the ignition temperatures of bitumen / nitrate mixture. Individual salts used in the BDF are tested. Especially contamination effects of Ni, Ag and Fe are evaluated.

In Chapter 5 we pay attention to the formation of explosive compounds in the bitumen nitrate mixture. The ignition temperatures of bitumen / Ni, Ag nitrate mixtures are measured at various heating rates.

Chapter 6 shows the flame propagation behavior of various condition of the bitumen / nitrate mixture. The possibility of the local fire expand to global fire is discussed.

In Chapter 7 we give the conclusion obtained in the present work.

The overview of this thesis



In other words, the purposes of the present study are itemized as follows.

1. Measurement of the self-ignition temperature.
 - To evaluate the potential hazard in bitumen nitrate / mixture.
2. Torque increasing effect of Fe(III).
 - Oxidation behavior of bitumen by $\text{Fe}(\text{NO}_3)_3$.
3. The formation of explosive compounds.
 - The relation between ignition temperature and heating rate.
 - The formation process of explosive compounds.
4. The flame propagation behavior.

- The relation between composition and flame propagation.
- The speed of flame propagation in the bitumen / nitrate mixture.
- The chemical composition of bitumen / nitrate mixture.

Table 1. 1 Significant Incidents in different kinds of nuclear facilities (1953-1993)

[1]

	Reprocessing	Enrichment	Conversion	Fuel fabrication	Others	Total
Criticality	9	-	-	2	-	11
Fire & Explosion	11	-	-	2	3	16
Release & Contamination	16	3	5	4	1	29
Others	1	1	-	-	-	2
Total	37	4	5	8	4	58

References

- [1] IAEA, Vienna, Austria, Significant incidents in nuclear fuel cycle facilities, IAEA-TECDOC-867, (March 1996)
- [2] Incident Investigation Committee, About the fire and explosion incident at the Bituminization Demonstration Facility of PNC Tokai Works (in Japanese), (Dec 15, 1997)
- [3] M. Nogami, M. Aida, Y. Fujii, A. Maelawa, S. Ohe, H. Kawai and M. Yoneda, Ion-Exchange selectivity of tertiary pyridine-type anion exchange resin for treatment of spent nuclear fuels, Nuclear Technol., 115 (1996) 293-297.
- [4] Y. Asano, N. Asanuma, N. Ito, M. Kataoka, S. Fujino, T. Yamamura, W. Sugiyama, H. Tomiyasu, K. Mizumachi, Y. Ikeda, Y. Wada and M. Asou, Study on a nuclear fuel reprocessing system based on the precipitation method in mild aqueous solutions, Nuclear Technol., 120(3) (1997) 198-210.

2. Fire hazards in the nuclear reprocessing facilities

2.1. Introduction

It is well recognized that the bituminized product is a mixture of organic compound and nitrates. In the USA and Russia, the accidents happened in the reprocessing plants or/and the relating plants resulting from the run-away reaction between organic compounds and nitrates. It is pointed out that there are a lot of possible hazardous factors in these accidents. Several accident reports will be introduced and show how to prevent the accidents in the following. It is noticed that the general trends of the accidents of the reprocessing plants or/and the relating plants.

Plant	Note
Hanford Waste Tanks	To prevent the accidents
Chelyabinsk-65	Serious accident report
Savannah River Plant, Tomsk-7	Red-oil incidents in reprocessing
Savannah River Plant Waste Tanks	To prevent the accidents
Tokai Bituminization Facility	Accident analysis

2.2. Hanford Waste Tanks (Watch out list)

At the Hanford Site of U.S Department of Energy's (DOE), radioactive and chemically complex waste was stored in the Site's 177 underground storage tanks. This site is the largest liquid waste storage facility in the world. Solid, liquid and sludge-like wastes are contained in 149 Single-Shell Tanks (SSTs, Fig. 2.1) and 28 Double-Shelled Tanks (DSTs). The average composition of supernatant and sludge are listed in Table 2.1 [3]. The 99% of radioactivity resulted from ^{137}Cs and ^{90}Sr . The major waste sources were from T&B plant, PUREX plant

2. Fire hazards in the nuclear reprocessing facilities

and REDOX plant [9]. The radioactive ^{137}Cs was precipitated out of the solution by adding potassium ferrocyanide ($[\text{K}_4\text{Fe}(\text{CN})_6]$) and nickel sulfate (NiSO_4). The radioactive ^{90}Sr was precipitated as SrF_2 out of the solution by adding sodium fluoride (NaF). In this process 93% of ^{137}Cs and 90% of ^{90}Sr can be removed in the solution. Before the acidic waste was discharged to the tanks, it was neutralized with sodium hydroxide (NaOH) because the acid would corrode the carbon-steel tank. In this process a large quantity of sodium hydroxide was added. The pH of the solution was adjusted in the range from 12 to 14. Recently, a lot of huge waste tanks have two major problems.

The first problem is that almost all the SSTs have a liquid waste leakage problem. The 50% of SSTs have already been corroded and some leakage has occurred. The DSTs of a high corrosion resistance type have been constructed and the waste liquid was moved from the SSTs to the DSTs. The liquid waste in the container has three layers, i.e. sludge, slurry and liquid. The movement and cleanup of sludge is very difficult and robotic arms are being used to cut, dig, and lift wastes.

The second problem is that these tanks have an explosive hazard [4,10,11]. To keep safety, these tanks are strictly observed by US DOE. If $[\text{Fe}(\text{CN})_6]^{4-}$ reacts with NO_3^- or NO_2^- ions, highly strong exothermic reaction will occur. Thus the concentration of $[\text{Fe}(\text{CN})_6]^{4-}$ is monitored and the tanks are observed not to exceed 93°C . However, the temperature does not rise up to 100°C because of water medium, and the existence of ferrocyanide ion cannot be a dangerous factor at the normal condition. Ferrocyanide is not a problem by another reason. Studies show that it will be converted into less reactive chemicals when being in contact with the tank waste.

From the viewpoint of flammable gases, total organic carbon (TOC) is monitored carefully [4,10,11]. TOC refers to all compounds containing carbon except carbonates (CO_3^{2-}) and carbon dioxide (CO_2). The high concentration of organic compounds in a tank is a safety problem because these compounds could act as “fuels” when mixed with “oxidizers” such as nitrates (NO_2^-) and nitrates (NO_3^-) at temperature higher than 221°C . The safety limit is assumed to be 3wt% of the total organic carbon. However, twenty SSTs contain organic compounds in amounts greater than the safety limit.

As of 1998, temperature of 10 tanks are ranging between 60 and 84°C . These tanks can be included on the watch list for several reasons:

- Highly flammable gas (for example, hydrogen) concentrations

2. Fire hazards in the nuclear reprocessing facilities

- Potentially explosive concentrations of ferrocyanide
- Potential for flammable organic nitrate reactions
- High temperatures that could dry out waste and degrade the concrete dome of the SSTs.

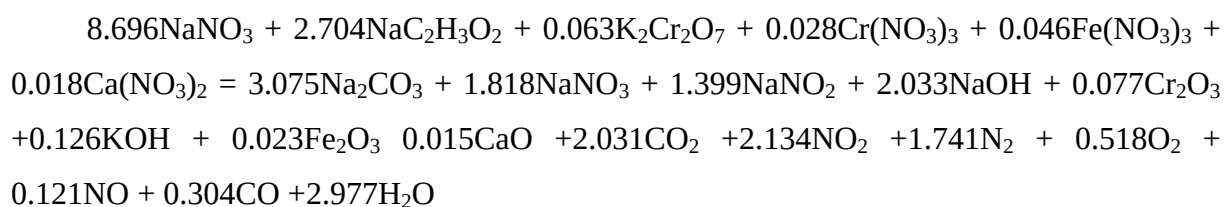
2.3. Chelyabinsk-65 (Waste Tank Facilities accident in 1957)

On 29 September in 1957 the radiation incident in the waste storage facility of a radiochemical plant occurred. This accident was the most serious fire and explosion incident relating to nitrate salts. It is recognized to be an explosion in the storage facility for high-level waste from production of weapon-grade plutonium. In spite that this accident is so serious and of a large scale, the summary of the accident had been veiled until recently because its facility is related to a weapon development. However, Dr. Zhores Medvedev who defected from USSR talked about this accident [12,13]. The prediction and hypothesis of this accident was published on the famous scientific journals between 1979 and 1980[14-17]. No report had appeared from USSR for a long time. In 1989, however, a public report was released from the USSR governmental committee and the world-wide accident research work was done. Due to the damage of the cooling system or other safety system in a high-level waste storage facility, superheating of the slurry or solid residue in the tank occurred, exciting an explosive reaction between the nitrates and organic ingredients of the waste (acetates or solvents) or detonation of the ammonium nitrate. In order to prevent chemical explosion, the tank was cooled using heat exchangers placed on the inner wall of the storage facility. In 1956, a heat exchanger in one of the storage facilities was jammed due to failure. The calculation done by specialists at the plant shows that even in the absence of cooling, the wastes would be stable (This calculation proved to be incorrect.)

In 1995, the governmental accident report [18] was published by the Russian Federal Nuclear Center. The exploded tank storage consisted of a welded cylindrical tank with a plane bottom without a cover(Fig. 2.2). Its outside diameter was 8 m and the height was 6 m. The tank made of stainless steel (13mm thick) was placed in a separate canyon of reinforced concrete having a diameter of 9 m and a depth of 7.4 m. The working volume of the exploded

2. Fire hazards in the nuclear reprocessing facilities

tank was 250 m^3 . Approximate content of the main chemical components of the poured solution is indicated on Table. 2.2. The tank storage contained radioactive elements, the decay of which was accompanied by considerable energy release: $8.5 \times 10^4 \text{ kcal/h}$ (at the beginning of the storage) $6.8 \times 10^4 \text{ kcal/h}$ (prior to the explosion). This energy release led to warming up the tank, to water evaporation and then to thermal explosion of the dry “sediment” of the salts. Ability of the “sediment” salts to the chemical explosion under heating up to 350°C was verified in experiments performed at PA “Mayak” soon after the accident. Using the simulated sediment sample, the explosion took place at 360°C . It seemed that the chemical reaction occurred as follows.



In this experiment $Q=270 \text{ kcal/kg}$ of heat was released during explosion of the “sediment”. We must account for the fact that the explosion was initiated at rather high preheating of the “sediment” due to energy release of the radioactive isotopes present there. The internal energy was $Q_T = 90 \text{ kcal/kg}$. This energy should be accounted for in the effective explosion energy release:

$$Q + Q_T = 270 \text{ kcal/kg} + 90 \text{ kcal/kg} = Q_{\text{eff}} = 360 \text{ kcal/kg}$$

Considering the mass of the exploded “sediment” was 70-80 t, we obtain the value of the effective energy release of the explosion.

$$E_{\text{eff}} = (25+29)\text{t TNT} = 54 \text{ t TNT}$$

The characteristics of the destruction can be used for assessing energy release of the explosion: (1) Degree of destruction of the exploded canyon; (2) Distance which the canyon cover was thrown; (3) Distance of stones which were scattered from the explosion epicenter; (4) The fact that the guard was not injured; (5) Data on the character of nearby buildings destruction; (6) Data on the character of the building windows destruction;

$$8\text{t} < E_{\text{eff}} < 42\text{t TNT}.$$

Summarizing the described assessments of the explosion energy release by the destruction pattern caused by it, we can assume that the available data allow to make only rather rough assessments of the energy release; This is consistent with the much more

substantiated value of the energy release obtained on the basis of the experiments performed and analysis determining calorificity of the exploded “sediment”.

2.4. Savannah River Plant (Accident of uranium conversion process, 1975)

Depleted U is separated from Pu by the PUREX process at the Savannah River Plant(SRP). Uranyl nitrate solution is transferred to facility called the A-Line (Fig. 2.3), where the solution is concentrated by evaporation to molten uranyl nitrate hexahydrate. The plant has mainly two processes. One is that the uranium solution is evaporated to yield molten $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and crystal water is removed. The other is that $\text{UO}_2(\text{NO}_3)_2$ is heated and converted to UO_3 powder. On Feb. 12, 1975, after 20 years of A-Line operation without a major incident, uncontrolled reaction occurred [5,19] during conversion of molten $\text{UO}_2(\text{NO}_3)_2$ to solid UO_3 . A rapid chemical reaction occurred in a denitrator and expelled the contents, including combustible gases, into the process room. During heating of the denitrator contents, the organic material decomposed rapidly between 170°C and 210°C, emitting combustible and noncombustible gases that ejected the denitrator contents into denitrate room. The gas collected at the ceiling and ignited with a low explosive force. The accident process was described as follows.

- 1 When flushing of silica gel column began, tank S-1-9 and S-1-8 contained a solution of 400 gU/liter at a density of 1.56 g/ml. Floating on top was a layer of $\text{UO}_2(\text{NO}_3)_2(\text{TBP})_2$ at a density of 1.45 g/litter.
- 2 The flushing of the silica gel column produced a solution containing ~250g U/liter with a density of 1.3g/liter. This yielded a three-layer striated system in tank S-1-9, with the organic layer in the middle.
- 3 The dense layer was moved to a hydrate evaporator (C-2-1 $\Leftrightarrow$ C-2-3). The hydrate evaporator was heated by steam at a pressure of 170 kPa. Thus, the temperature did not exceed 129°C. Therefore the organic was not decomposed but dropped to the denitrators.
- 4 Denitrator C-3-4, containing ~1175 kg of $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and ~190kg of $\text{UO}_2(\text{NO}_3)_2(\text{TBP})_2$, was heated more slowly than usual. When the denitrator skin

2. Fire hazards in the nuclear reprocessing facilities

temperature controls were reset from 250 to 400°C, the temperature of the denitrator contents was estimated at 150 to 160°C.

- 5 Thermal decomposition of the $\text{UO}_2(\text{NO}_3)_2(\text{TBP})_2$ began at $\sim 170^\circ\text{C}$. The gases released were NO, N_2O , NO_2 , O_2 , H_2O , butene, butanol, and possibly BuNO_x ($x=1,2$, or 3) compounds. The estimated gas release was about 500 m^3 STP.
- 6 This rapid release of gases ejected the denitrator contents into the room. The gases collected at the ceiling, ignited, and generated a pressure that blew out the walls. The pressure necessary to cause the transit damage observed is less than 0.5 atm.

2.5. Tomsk-7 (Red oil accident in 1993)

On April 6, 1993, an explosion [6,20] caused significant damage to the PUREX reprocessing plant of the Siberian Chemical Combine at TOMSK-7, Russia. The accident is called a red-oil accident. The ruptured tank was made of stainless steel and identified as AD-61602/2. Its total volume was about 31 m^3 (31000L). Fig.2.4 shows tank AD-6102/2 schematically with its instrumentation and fitting. The first was approximately 4000L of a solution derived from first-cycle cleanout. It contained 1.5 M of nitric acid and 30 g/L (0.13 M) of uranium and an unknown amount of organic material derived from accumulations at the aqueous-organic interface in the extraction column. Furthermore, 19500 L of recycle concentrate-containing 440 g/L of U and 320g of Pu was added to this tank. This solution was contaminated by fission products as a result of their incomplete removal during the first cycle of separations. It was prepared by evaporating two batches of uranium product solution with a total volume of 88000 L to 22% of their original volume.

Early in the morning of April 6, the first-cycle cleanout solution was in Tank AD-6102/2, and a 12000 L portion of freshly evaporated concentrate was added to it. The liquid temperature was measured to be 78°C at the bottom of the tank. Cooling coils on the tank were then operated to bring the temperature indication below 50°C .

- At 9:30 A.M., 7500 L of freshly evaporated concentrate was added. The total amount is 23500 L and the temperature of the bottom was between 45 and 50°C
- At 10:30 A.M., 1500 L of 14.2 M nitric acid was added to the tank. The density of nitric acid was 1.39, which was less than that of uranium solution (about 1.6).

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Thus the nitric acid may have been pooled on top of the uranium solution with very little mixing.

—Beginning at about 12:45 P.M., brown fume, presumably nitrogen oxides, was observed from the canyon stack. A positive pressure reading was observed.

—At about 12:58 P.M., the tank ruptured explosively, lifting the shield plug from the chamber and allowing all the volatile material to enter the service area overhead.

The reaction has been attributed to the runaway reaction of concentrated nitric acid with organic material floating on the aqueous layer within the tank. The following actions and conditions may have been contributed to the occurrence:

- 1, The concentration of the acid added was higher than normally used.(14.2 M vs. a normal administrative limit of 12 M)
- 2, Allowing TBP-containing organics to stand for months in the presence of acid and radiation must have caused partial hydrolysis, with the likely accumulation of butyl nitrate, which is formed during the nitric-acid catalyzed hydrolysis of TBP:
$$\text{O}=\text{P}(\text{--O--C}_4\text{H}_9)_3 + 3\text{H}_2\text{O} \rightarrow \text{O}=\text{P}(\text{--OH})_3 + 3\text{C}_4\text{H}_9\text{OH} \quad (1)$$
$$\text{C}_4\text{H}_9\text{OH} + \text{HNO}_3 \rightarrow \text{C}_4\text{H}_9\text{ONO}_2 + \text{H}_2\text{O} \quad (2)$$
- 3, From the nitration of diluents, more reactive organic compounds may have accumulated.
- 4, Inadequate venting of the vessel appears to have been a contribution factor. In the laboratory studies, the nitric acid-TBP reaction will not accelerate if the system is adequate

In this accident we should mention item 4 above mentioned. For the items from 1 to 3, these causes have already been known in relation to the accident. Above 125°C the reactions (1) and (2) occurred rapidly after the bulk of the water was removed and solids were formed from the uranyl nitrate solution. In the TOMSK-7 event, the solution was warm but well below 120°C. As pressure builds up in an unvented or inadequately vented system, the boiling temperature increases and evaporation is no longer effective in removing the reaction heat. Studies of this system using AIChE DIERS method [21-27] have proved a basis for establishing minimum venting. A number of DIERS studies of TBP-nitrate mixtures [7], using various reaction volumes and vent size, were used to drive Fig. 2.5. This figure shows that

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above a critical mass/vent area ratio the potential pressurization increase very rapidly. The volume of the reacting organic materials is not certain, but estimates were used to establish the region possible Toms-7 condition shown in Fig.2.5. This clearly overlaps the region of potentially large pressure excursions. This means that this device contains miss architecture and has fatal defects of architecture. This structure has a destiny to explosion.

2.6. Explosive compounds in Savannah River Site Waste Tank Facilities

The Savannah River Site (SRS) has two-high nuclear waste storage areas. These areas are located in F area and H area adjacent to the separations canyons. The storage facility consists of 51 underground carbon steel storage tanks, 4 waste evaporators and underground transfer lines. The waste composition of sludge and supernatant is listed in Table 2.3 and Table 2.4. A comprehensive list of conceivable explosive compounds is provided in Appendix 1 and Appendix 2. D.T.Hobbs [3] reported that the fourteen classes of explosive compounds identified as conceivably being present in tank farm operations, and nine classes (metal fulminates, metal azides, halogen compounds, metal-amine complexes, nitrate/oxalate mixtures, metal oxalates, metal oxohalogenates, metal cyanides/cyanates, and peroxides) are not a hazard because these classes of compounds cannot be formed or accumulated in sufficient quantify, or they are not reactive at the condition which exists in the tank farm facilities.

Three classes (flammable gases, metal nitrides, and ammonia compounds and derivatives) are known to have a potential to build up concentration at which observable reaction might occur.

To prevent the formation of explosive silver compounds, the introduction of silver into waste tanks was discontinued in 1970. Mercury has been used and continues to be used in separations as a catalyst in the dissolution of aluminum.

(a) Flammable gases

Hydrogen is produced in the waste storage tanks as a result of the radiolysis of water. Hydrogen monitors are installed on the waste tanks. These monitors are set to alarm when the hydrogen concentration reaches 10% of the lower flammability limit (LFL). Other flammable

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gases that could conceivably be produced in the waste tanks include methane, ethane, ethylene, and n-butanol. Because of the very low organic content and the active ventilation system on each tank, the generation of the flammable vapor mixture is not generated.

(b) Metal Nitrides

In 1970, when personnel stepped on dried waste deposits, popping noises were heard at the Tank 21H feed-jet enclosure and the Building 242-H evaporator cell. An investigation of the incident implicated silver nitride as the cause of the explosive deposits. Silver nitride is formed by the decomposition of silver diammine solutions. To prevent the formation of explosive compounds, the introduction of silver into waste tanks was discontinued in 1970. Since this administrative control has been in place, no other incidents of this type have been observed in the tank farm operations. Silver-containing waste has been removed and processed for disposal during the ITP(In-Tank Precipitations) and SP(Sludge Processing) operations

(c) Ammonia compounds and derivatives

Ammonium nitrate, ammonium nitrite and ammonia/air mixture are well documented explosive hazard. In 1976 a large quantity of ammonium nitrate(3100 Kg) was discharged to waste tanks. An investigation concluded that the source of the ammonium nitrate was the vessel vent filters of the F canyons [28]. The filters were flushed with water to remove the ammonium nitrate and the solution was transferred to the tank farm. The procedure to prevent the formation of explosive ammonia/air vapor limited the concentration of ammonia nitrate to < 2.5 wt%.

Two other ammonia derivatives, hydrazine and hydroxylamine were used as reductants in the chemical separation process and could conceivably be in the high-level waste. If an insufficient amount of nitrite were added to destroy the hydrazine during chemical separations, hydrazine would rapidly react with oxidants or metal ions in solution when the waste was neutralized. Alkaline solutions of hydroxylamine are unstable and decompose to give a mixture of nitrous oxide ammonia. Thus, significant amounts of hydroxylamine would not be expected to be in SRP waste.

2.7. Fire and explosion in the bituminization facility of Tokai reprocessing plant on March 11,1997

2.7.1. Bituminization facility

The bituminization demonstration facility (BDF) gives solidification treatment to low-level liquid waste from the Tokai Reprocessing Plant (TRP, Fig. 2.6). The waste in the receiving tank (V21) is transferred to reaction vessels (V30 and 31) in each batch operation. The chemicals are added to the reaction vessel as a pretreatment of the waste. Sodium carbonate and barium hydroxide are added for coprecipitation of strontium. Nickel sulfate and potassium ferrocyanide are added to the reaction vessel for the coprecipitation of cesium. To decrease the volatilization of iodine, sodium iodate, sodium sulfite and silver nitrate are added to the reaction vessel. Then, the waste is transferred to the feeding vessel (V32 and 33) and fed into the extruder (Fig. 2.7) with a double airlift. At the first zone, heated bitumen material is fed, water is vaporized at 4th-6th zone and the mixture is discharged at 8th zone to be filled in a drum. The normal feed rate of waste solution is 200 l/h. In the extruder the waste bitumen is kneaded. The resulting mixture is poured into a drum on the turntable. One drum is filled up in about two hours. About ten drums of bituminized waste are produced in a batch.

2.7.2. Incident process

The sequence of the incident was as follows [29].

At 10:06 ; An operator found a flash in the filling room and observed a 2m-high pillar of fire in a drum. After ten seconds all drums seen through a shielding window emitted pillars of fire. Fire and temperature detectors gave an alarm and again at 10:08.

At 10:10 ; An auto fire alarm was on. The operator could not see the fire because the inside of the room was filled with smoke.

At 10:12 ; The water sprays started to extinguish the fire. After one minute, the operator stopped the water spray because he did not see the fire in the room. He saw the smoke leaking from the penetration of the manipulator.

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At 10:13 ; A β -dust monitor of the conveyer room gave an alarm. In the control room, the ventilation alarm was on. An operator pushed the emergency stop button of the extruder.

At 10:14 to 10:18 ; A β -dust monitor gave an alarm in the maintenance operation room and the cask storage room. At 10:18, the lamp of the cell ventilation blower in the control room showed a stop of airflow, and an exhaust blower for the building ventilation started to operate.

At 10:23 ; All the blowers were put off.

At 20:04 ; An explosion occurred. An area γ -monitor in the maintenance operation room gave an alarm. After explosion, the thermocouples in the poring tube indicated a temperature rise two times during two and a half hours. According to the monitoring camera outside the building, the smoke stopped flowing from the window at around 23:30.

2.7.3. Environment effect

The radioactivity released from the BDF was studied by two methods; Sasaki *et al.* [29] reported that one was the migration behavior from the fired drum through the building and the other was the environmental monitoring. The released activity to the environment was estimated to be of the order of 10^{-3} GBq for α -nuclides and several GBq for β -nuclides. The committed dose equivalent was evaluated to be 10^{-3} to 10^{-2} mSv. In the latest report Igarashi *et al.* [30] wrote that the $^{134}, ^{137}\text{Cs}$ air concentration was about 100 and 10 mBq m^{-3} , respectively. This result suggested that there was little radiation exposure of the residents in the area. The average ^{137}Cs air concentration during this period was about two orders of magnitude higher than that of “baseline” air ($\text{sub-}\mu\text{Bq m}^{-3}$) during February to April 1997, which was measured by ultra-low background γ -spectrometry. By a simple calculation of the measured data using a Gaussian plume model, they estimated the minimum emission of the radioactivity by the PNC accident was in the range from 60MBq to 600MBq.

2.7.4. Abnormal condition in operation

There were mainly three abnormal conditions [31] different from the standard operation in B29 of campaign 97M46-1. These abnormal operating conditions may be related to this accident.

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The first abnormal operating condition was as follows: There was a lot of precipitation in the V21 receiving vessel due to previously accumulated solid waste. An air sparger was used to agitate the whole waste in the V21 vessel to extract the sample. Normally the waste was transferred to the next vessel after one night. At this time, however, a few minutes later, transfer of the waste to the V31 reaction vessel was initiated. As a result, a large amount of precipitation was mixed with liquid waste.

The second abnormal one was as follows: the receiving vessel (V21) intermittently received 1m^3 of phosphoric acid wastes (ST wastes). Normally the concentration of the PO_4^{3-} ranged from 5 mg/L to 1.4 g/L, however, in this case the measured concentration of PO_4^{3-} was about 7.7 g/L.

The third abnormal one was as follows: the waste was normally fed to the extruder at the rate of 200 L/hr. However, in campaign 97M46-1 the feed rate was changed to 160 L/hr after B26. Consequently the evaporation occurred earlier than at the normal condition and recrystallization may have occurred in the process.

2.8. Research activity movement of Tokai bituminization accident

2.8.1. Introduction

The cause of accident has not been definitely clarified. There are a lot of research activities relating to the fire and explosion accident in the Tokai Works. The research activities are mainly classified into two parts. One is on the physical heating. The other is on the heating resulting from chemical reactions. The accident occurred because these factors were intricately related with each other. It is difficult to conclude the cause of the accident. We will rearrange these research activities. A lot of researcher performed accident analysis, we should pay attention to the trends of research works.

2.8.2. Exothermic reaction from physical factor

- Friction Heat in the extruder

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If higher resistance on the shaft occurred in the extruder, the electric current increased and made the rotation increase. In this case the energy of excess electric current should have been converted to the heat energy. The friction resistance would produce the friction heat. It is reported that, if the torque is 30% higher than the base, it leads to a temperature increase in the extruder [32].

2.8.3. Exothermic reaction from chemical reaction

(a) Contamination of TBP, DBP or antifoaming agent

If a lot of organic compounds such as TBP, DBP or antifoaming agent are contaminated in the bituminized product, the exothermic reaction will occur. On the fire accident at eurochemic plant in Belgium on December 15 [33], 1981, TBP or its degradation products like di- and monobutyl phosphate must have been present in the hazardous slurry SP29400, which was related to the fire accident with a high degree of probability. They also mention that it is impossible to identify one compound alone that could have provoked the fire incident. It is more likely that the hazardous components should have been identified in the hot waste feed streams, which were concentrated by evaporation to the hot waste concentrate batch used for the preparation of the hazardous slurry SP29400, i.e.,

- The deterrent and radiac Wash decontamination reagents.
- The bituminous oil fractions.
- The heel residues of vessel 543 containing TBP and/or its degradation products, and possibly.
- Ion exchanger beads and nitrated organic compounds.

In the accident of PNC Tokai works, Koyama *et al.* [32] reported that the concentration of oily compounds such as TBP and/or BDP was so low, which was several hundred ppm in the waste solution. The contamination of abnormal organic compounds seemed not to be recognized. The amount of added chemical reagent was normal. Thus the accident did not result from contamination of added chemical reagent or abnormal organic compounds.

● Fine structure effect of salt particles

Hasegawa *et al.* reported that the reaction between bitumen and NaNO_3 or NaNO_2 was estimated using SETARAM C80D thermal analysis at the heating rate of $0.01^\circ\text{C}/\text{min}$ with various diameters of salt particles. The sample containing quite small salt particles ($<53\mu\text{m}$)

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has higher reactivity than the sample containing large diameter salts (mainly 0.29-0.43mm diameter). The geometrical structure of the salt particles in the bituminized product is significant for controlling the diffusion rate.

- Effect of overabundance of NaHCO_3

Hasegawa *et al.* [9] reported that if NaHCO_3 in the simulated sample decomposed, CO_2 and H_2O were generated. Consequently, many micro pores were formed and salt particles became porous, because of the gases escaped from the salt particles. The chemical reaction and diffusion of the interfacial reaction between salts and asphalt is a rate-determining step of an overall reaction. The structure of porous salt particles (honeycomb structure) would greatly accelerate the diffusion step of the interfacial reaction.

- Effect of overabundance of NaH_2PO_4

Hasegawa *et al.* [34] reported that the mixture of bitumen and NaH_2PO_4 was evaluated using C80D thermal testing method. The phosphate may have no promoting effect of blowing reaction of asphalt. Dehydration reaction of phosphate is indicated by:



As this reaction proceeds at 400°C , this reaction did not occur in the extruder, because the extruder is operated below 195°C .

- Effects of pH value

The waste solution was neutralized by using NaOH , $\text{Ba}(\text{OH})_2$ and HNO_3 . The pH value was adjusted to 9.1. Hasegawa *et al.* [35] reported that thermal analysis of simulated bitumen sample was conducted using SETARAM C80D. The pH value of simulated sample was changed between $\text{pH}=8.5$ and $\text{pH}=9.87$. The deviation of pH value slightly affects the reactivity of the sample. Its effect is not so large nor so definitive.

- Blowing effect of the bitumen

To harden bitumen, air is introduced into the bitumen under $200\text{-}300^\circ\text{C}$ and the blown asphalt is thus produced in industry. This reaction utilizing the oxidation and polycondensation is called “blowing reaction”. The blowing reaction is exothermic reaction. The blowing reaction is suspected of causing of this accident. As three factors, (air, high temperature and catalysis) promote the blowing reaction, these factors should be checked. Air may have been introduced into the extruder because the feed solution was 20% smaller than the normal condition and the lack of steam to prevent the air may have occurred. The temperature of the circumstance may have been higher than normal temperature (180°C).

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- Melting of nitrates (molten salt chemistry)

In the chemical reaction between ASP and salts, normally operating temperature is 180°C. At this condition ASP is liquid and the salts are solid where, it should be considered the chemical reaction between solid and liquid. The chemical reaction between solid and liquid must be very slow, because the migration of compounds through the liquid-solid (ASP/nitrates) interface is the rate-determining step for the overall chemical reaction. If solid salt is melted at higher temperature than the melting point (mp), which is called molten salt [8], the reaction speed between ASP and nitrates will be increased. Fig.2.8 shows the phase diagram of metal nitrates. In the case of (a) $\text{KNO}_3\text{-NaNO}_3$, the mp considerably decreases to 220°C. In the case of (b) $\text{NaNO}_2\text{-NaNO}_3$, (c) $\text{AgNO}_3\text{-NaNO}_3$, and (d) $\text{CsNO}_3\text{-NaNO}_3$, the lowest mp's of the eutectic mixture are 225, 210 and 90°C, respectively. As a not so large amount of CsNO_3 was contaminated in the waste stream, it is not reasonable to consider the case (d). While the mp of pure NaNO_3 is 320°C, the mp's of these nitrate mixtures are 100°C lower than that of pure NaNO_3 . As a lot of NaNO_2 and K^+ ion exist in the process stream, the exothermic reaction between the ASP and nitrate may quickly occur around the liquid-liquid interface or in these mixtures.

The piping materials of facility are based on the austenitic stainless steel. SS300 series of the austenitic stainless steel have a corrosion resistance. Normally the chromium makes a passive state and the corrosion does not proceed, but a lack of chromium occurs in case of formation of the chromium carbide, and the corrosion will proceed. Table 2.5 shows the chemical composition of the austenitic steels. These steels have a large amount of nickel. In SS304 8-10wt.% of the nickel is contained. If the corrosion proceeds, $\text{Ni}(\text{NO}_3)_2$ may be formed. Generally nickel is used as catalysis to promote the chemical reaction in the chemical industries. Thus the potential hazard may exist in the bituminization process.

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Table 2. 1 Hanford waste tanks stimulants used in degradation studies [1].

Compound	101-SY	107-AN	103-C
	g/L		
NaOH	27.5	40	-
NaNO ₃	52.2	325.5	11.9
NaNO ₂	63	73.85	45.6
Na ₂ CO ₃	22.3	132.5	42.4
NaAlO ₂	39.1	3.89	-
KNO ₃	3.37	5.45	-
Na ₄ EDTA	21.2	37.7	12.8
Na ₃ PO ₄ ·12H ₂ O	10.25	1.9	7.6
KCl	5.2	-	-
Na ₂ SO ₄	2.37	20	41.2
NaF	0.25	-	-
NaCOOCH ₃	-	60.6	-
Na ₂ C ₂ O ₄	-	59.9	20.7
NaCOOH	-	60.6	-
Fe(NO ₃) ₃ ·9H ₂ O	0.81	10.9	0.81
Cr(NO ₃) ₃ ·9H ₂ O	12.6	-	-
NaCl	-	5.85	-
Ni(NO ₃) ₂ ·6H ₂ O	-	-	0.58
pH	13.75	11.36	9.27
Density(g cm ⁻³)	-	1.46	1.12

Table 2. 2 Approximate content of the main chemical components of the poured solution in Chelyabinsk-65 facility [2].

Compound	Concentration
Sodium nitrate (NaNO ₃)	200 g/L
Sodium acetate (NaC ₂ H ₃ O ₂)	60 g/L
Potassium bichromate (K ₂ Cr ₂ O ₇)	5 g/L
Chromium nitrate of (Cr(NO ₃) ₃ ·9H ₂ O)	3 g/L
Ferrous nitrate (Fe(NO ₃) ₃)	3 g/L
Calcium nitrate (Ca(NO ₃) ₂)	0.8 g/L

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Table 2. 3 Average Composition of Sludge of Savannah River Plant Waste Tank (USA) [3].

Compound	Wt%	Compound	Wt%
Fe(OH) ₂	30.100	Al(OH) ₃	32.900
MnO ₂	5.100	Ni(OH) ₂	1.940
CaCO ₃	4.000	Zeolite	3.650
SiO ₂	5.870	NaOH	3.280
NaNO ₃	2.830	HgO	1.600
CaSO ₄	0.475	CaC ₂ O ₄	0.404
Ca ₃ (PO ₄) ₂	0.373	CaF ₂	0.101
NaCl	0.101	ThO ₂	0.576
PbSO ₄	0.141	Cr(OH) ₃	0.384
AgOH	2.03×10^{-2}	Cu(OH) ₂	0.112
Co(OH) ₂	6.06×10^{-2}	Zn(OH) ₂	0.293
Mg(OH) ₂	0.505	Carbon	9.81×10^{-2}
Group A	0.274	Group B	0.902
PuO ₂	3.68×10^{-2}	SrCO ₃	0.105
Y ₂ (CO ₃) ₃	6.91×10^{-2}	RuO ₂	6.62×10^{-2}
RhO ₂	1.40×10^{-2}	CsNO ₃	1.06×10^{-2}
BaSO ₄	0.151	UO ₂ (OH) ₂	3.400
NaI	1.01×10^{-2}		

Zeolite: 48.0 wt% SiO₂, 19.1 wt% H₂O, 18.6 wt % Al₂O₃, 4.1 wt% Na₂O, 10.2 wt% CaO.

Group A: Tc, Se, Te, Rb, and Mo

Group B: Ag, Cd, Cr, Pd, Tl, La, Ce, Pr, Pm, Nd, Sm, Tb, Sn, Sb, Co, Zr, Nb, Eu, Np, Am, and Cm

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Table 2. 4 Average Composition of supernatant of Savannah River Plant Waste Tank (USA) [3].

Compound	Wt. %
NaNO ₃	45.70
NaOH	7.30
NaNO ₂	18.50
NaAlO ₂	10.00
Na ₂ CO ₃	7.70
Na ₂ SO ₄	10.40
NaCl	0.31
NaF	2.03×10^{-2}
Na[HgO(OH)]	6.27×10^{-2}
Group A	1.31×10^{-3}
Group B	3.74×10^{-4}
Na ₂ PuO ₂ (OH) ₄	2.54×10^{-6}
UO ₂ (OH) ₂	1.66×10^{-4}
Na ₂ RuO ₄	5.11×10^{-3}
Na ₂ RhO ₄	5.24×10^{-4}
CsNO ₃	9.76×10^{-3}
Ba(NO ₃) ₂	1.64×10^{-5}
Sr(NO ₃) ₂	1.47×10^{-5}
Y(NO ₃) ₃	1.04×10^{-5}
NaI	2.95×10^{-5}
Tortal organic carbon ^a	7.30×10^{-2}

Group A: Tc, Se, Te, Rb, and Mo

Group B: Ag, Cd, Cr, Pd, Tl, La, Ce, Pr, Pm, Nd, Sm, Tb, Sn, Sb, Co, Zr, Nb, Eu, Np, Am, and Cm

^a Based on highest measured value for fresh waste receipt tank supernate samples (D.T. Hobbs, "Organic Content of Tank 33 and Tank 34 Supernate Samples", IWT-LWP-91-033, March 7, 1991).

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Table 2. 5 Chemical composition of austenitic stainless steel (Unit %)

Standard		Chemical composition (%)								
JIS	ISO	C	Si	Mn	P	S	Ni	Cr	Mo	Other
SUS201	A-2	≦0.15	≦1	5.50-7.50	≦0.06	≦0.03	3.50-5.50	16.00-18.00	-	N ≦0.25
SUS302	A-3	≦0.15	≦1	≦2.00	≦0.045	≦0.03	8.00-10.00	17.00-19.00	-	-
SUS303	14	≦0.15	≦1	≦2.00	≦0.2	≦0.15	8.00-10.00	17.00-19.00	≦0.6	-
SUS303Se	17a	≦0.15	≦1	≦2.00	≦0.2	≦0.06	8.00-10.00	17.00-19.00	-	Se ≧0.15
SUS304	11	≦0.08	≦1	≦2.00	≦0.045	≦0.03	8.00-10.50	18.00-20.00	-	-
SUS304L	10	≦0.03	≦1	≦2.00	≦0.045	≦0.03	9.00-13.00	18.00-20.00	-	-
SUS304N1		≦0.08	≦1	≦2.50	≦0.045	≦0.03	7.00-10.50	18.00-20.00	-	N 0.10-0.25
SUS304J3		≦0.08	≦1	≦2.00	≦0.045	≦0.03	8.00-10.50	17.00-19.00	-	Cu 1.00-3.00
SUS305	13	≦0.12	≦1	≦2.00	≦0.045	≦0.03	10.50-13.00	17.00-19.00	-	-
SUS305J1		≦0.08	≦1	≦2.00	≦0.045	≦0.03	11.00-13.50	16.50-19.00	-	-
SUS309S	13(1)	≦0.08	≦1	≦2.00	≦0.045	≦0.03	12.00-15.00	22.00-24.00	-	-
SUS310S	16(1)	≦0.08	≦1.5	≦2.00	≦0.045	≦0.03	19.00-22.00	24.00-26.00	-	-
SUS316	20,20a	≦0.08	≦1	≦2.00	≦0.045	≦0.03	10.00-14.00	16.00-18.00	2.00-3.00	-
SUS316L	19,19a	≦0.03	≦1	≦2.00	≦0.045	≦0.03	12.00-15.00	16.00-18.00	2.00-3.00	-
SUS317		≦0.08	≦1	≦2.00	≦0.045	≦0.03	11.00-15.00	18.00-20.00	3.00-4.00	-
SUS317L	24	≦0.03	≦1	≦2.00	≦0.045	≦0.03	11.00-15.00	18.00-20.00	3.00-4.00	-
SUS321	15, 11(1)	≦0.08	≦1	≦2.00	≦0.045	≦0.03	9.00-13.00	17.00-19.00	-	Ti ≧5xC%
SUS347	16,12(1)	≦0.08	≦1	≦2.00	≦0.045	≦0.03	9.00-13.00	17.00-19.00	-	Nb ≧10xC%
SUS384	D25(2)	≦0.08	≦1	≦2.00	≦0.045	≦0.03	17.00-19.00	15.00-17.00	-	-
SUSXM7	D26(2)	≦0.08	≦1	≦2.00	≦0.045	≦0.03	8.50-10.50	17.00-19.00	-	Cu 3.00-4.00

2. Fire hazards in the nuclear reprocessing facilities

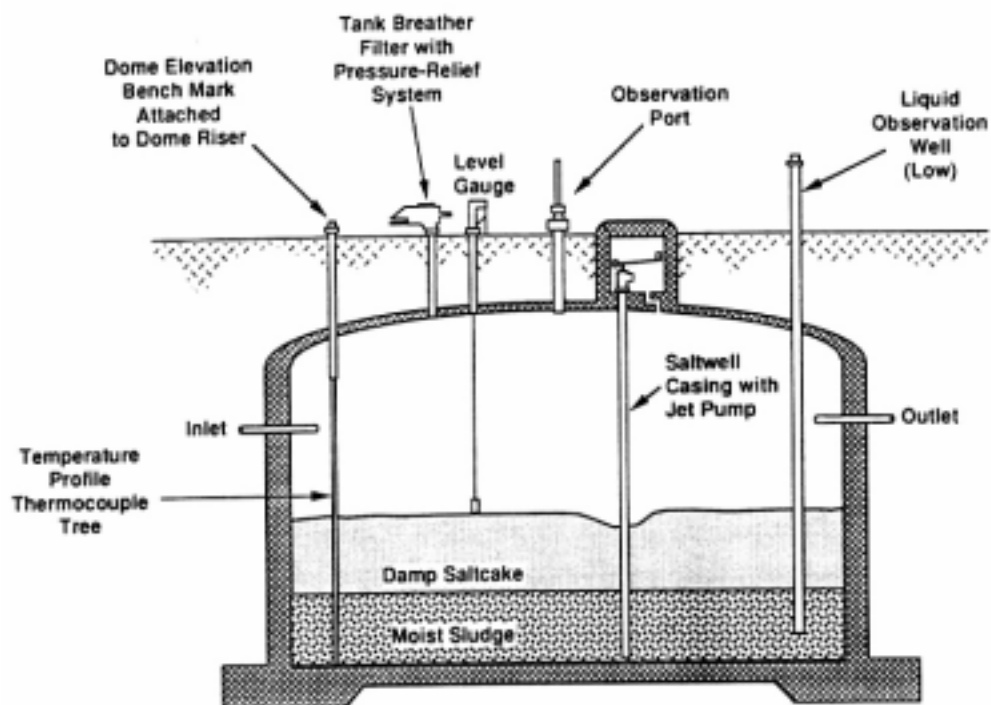


Figure 2. 1 Hanford Waste Tank of typical Single-Shell Tank (SST) [4].

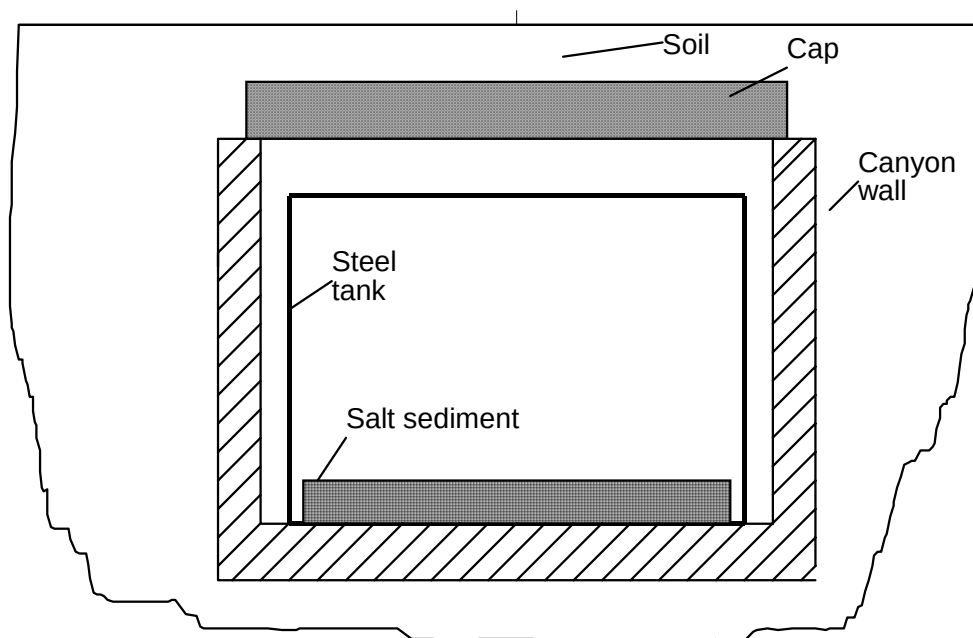


Figure 2. 2 Schematic drawing of exploded tank storage of wastes in “Mayak” (Chelyabinsk65, Russia) [2].

2. Fire hazards in the nuclear reprocessing facilities

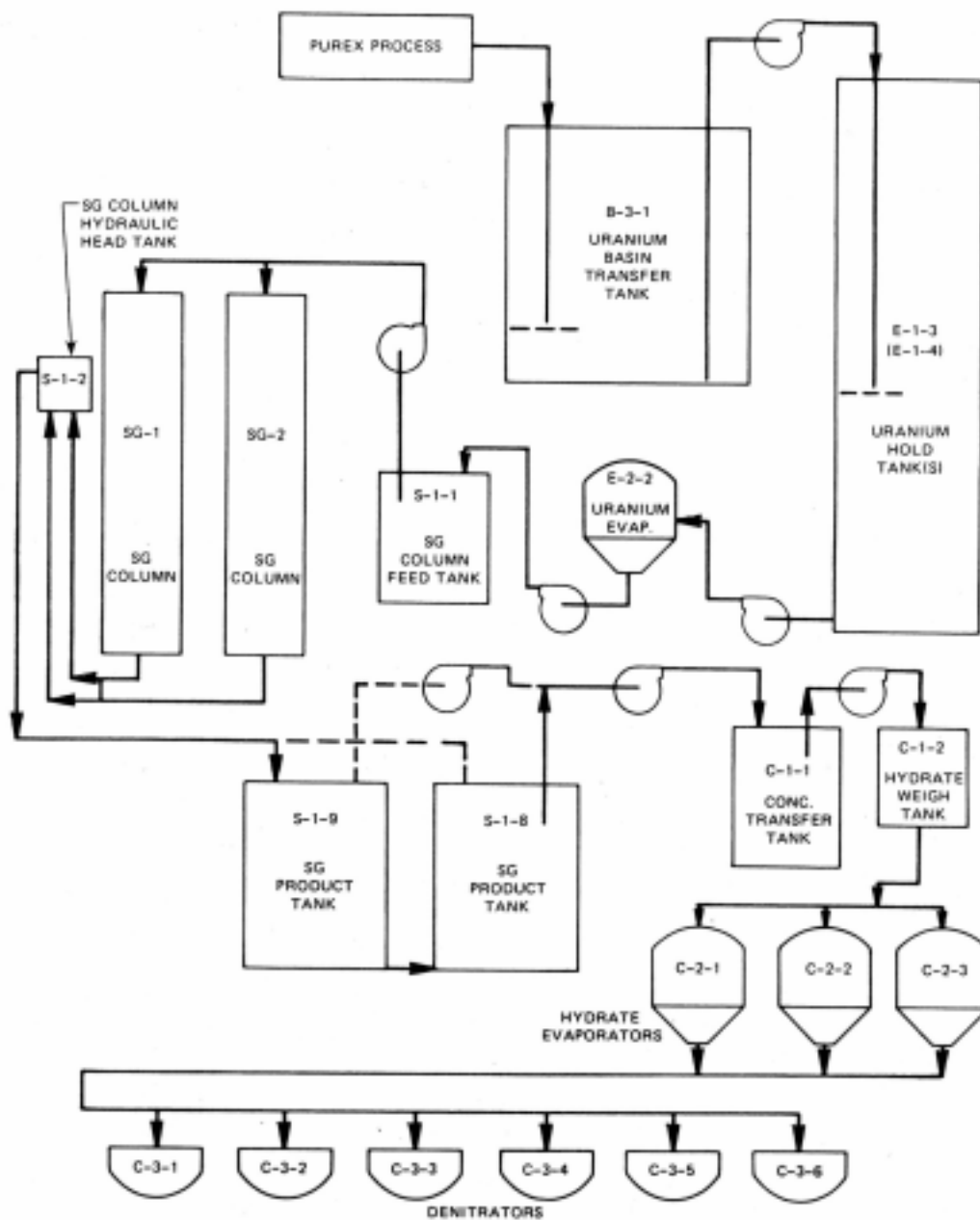


Figure 2. 3 Simplified process diagram of the A-Line facility of the Savannah River Plant [5].

2. Fire hazards in the nuclear reprocessing facilities

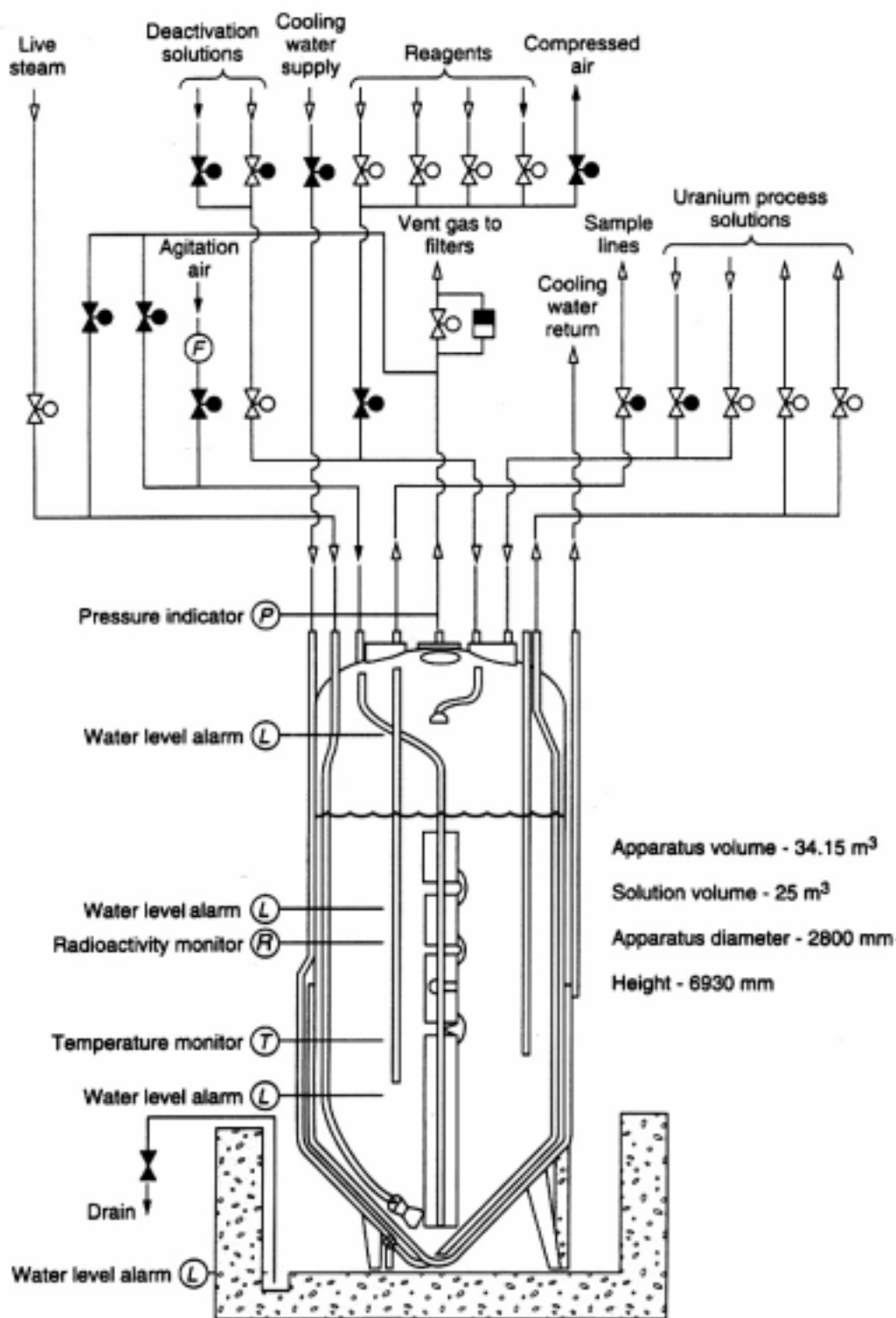


Figure 2. 4 Schematic drawing of vessel AD-6102/2 showing connection and monitors of TOMSK-7 [6].

2. Fire hazards in the nuclear reprocessing facilities

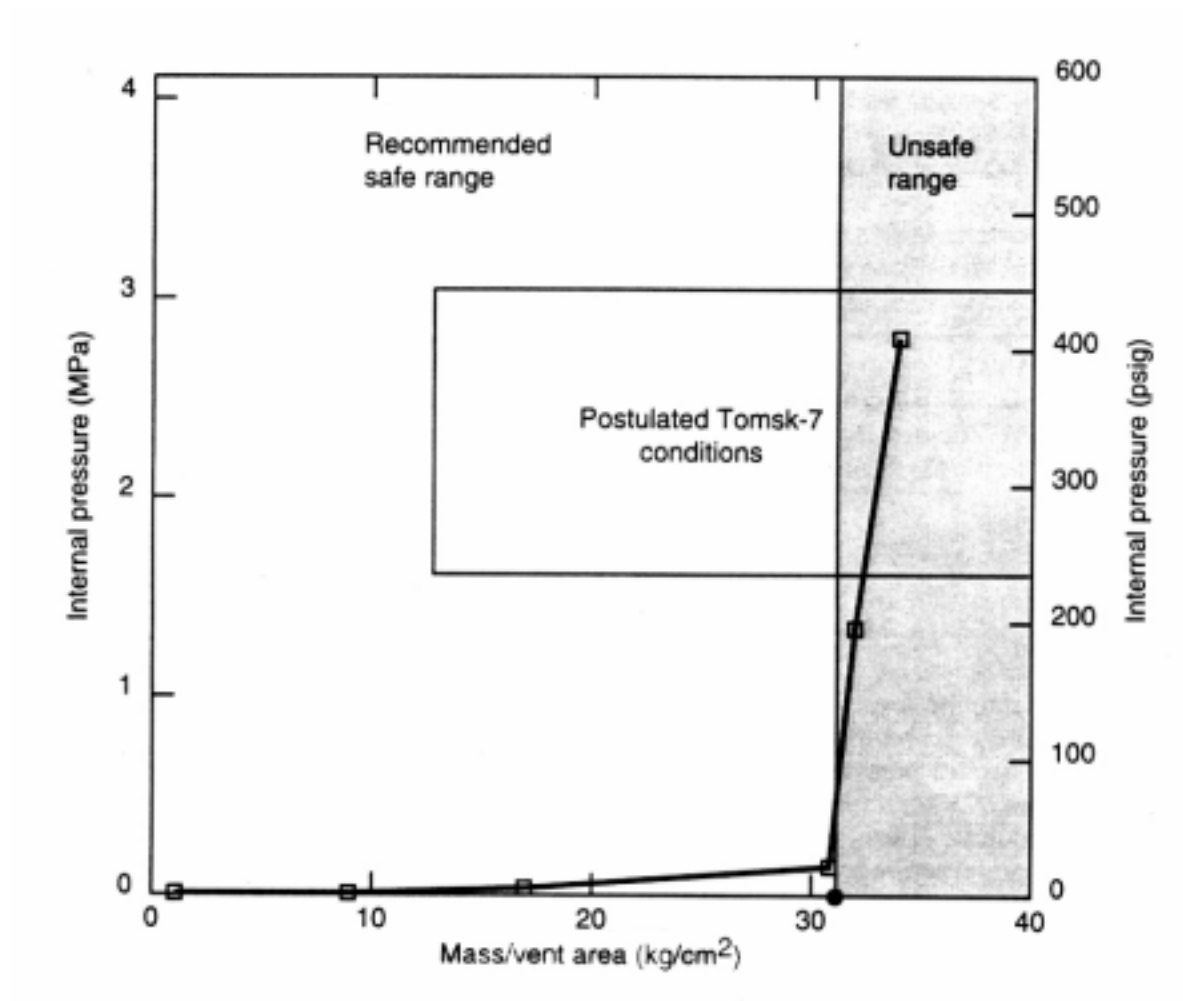


Figure 2. 5 Effect of vent size on internal pressure in heated TBP-nitric acid system [7].

2. Fire hazards in the nuclear reprocessing facilities

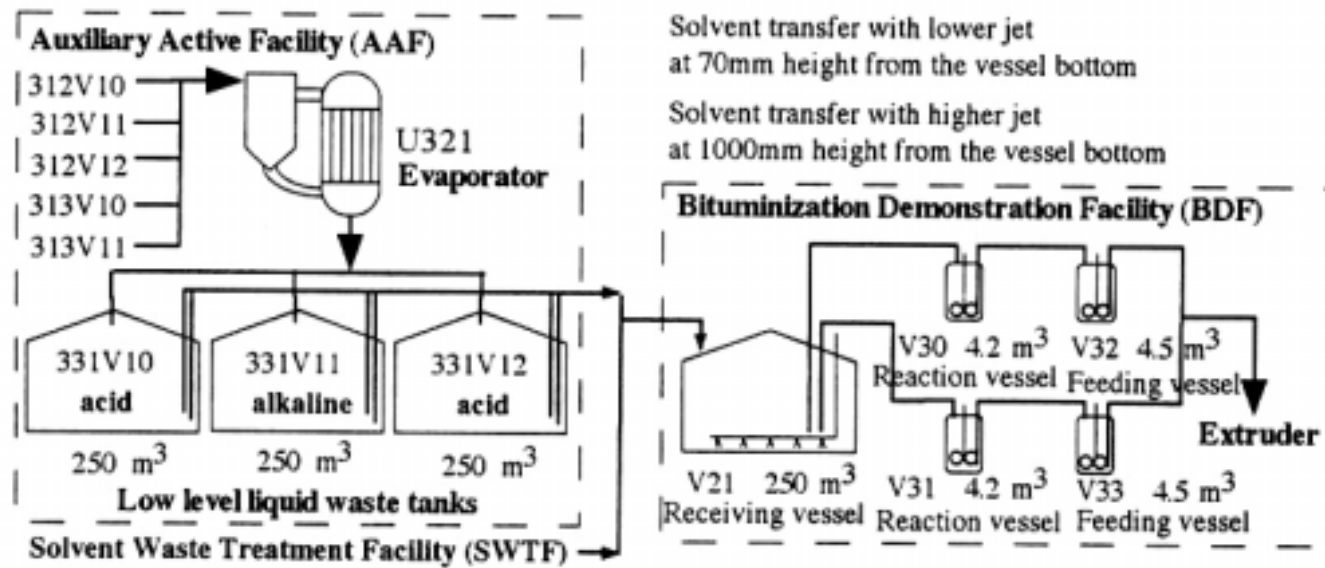


Figure 2. 6 Flow chart of the low-level waste solution to bituminize.

2. Fire hazards in the nuclear reprocessing facilities

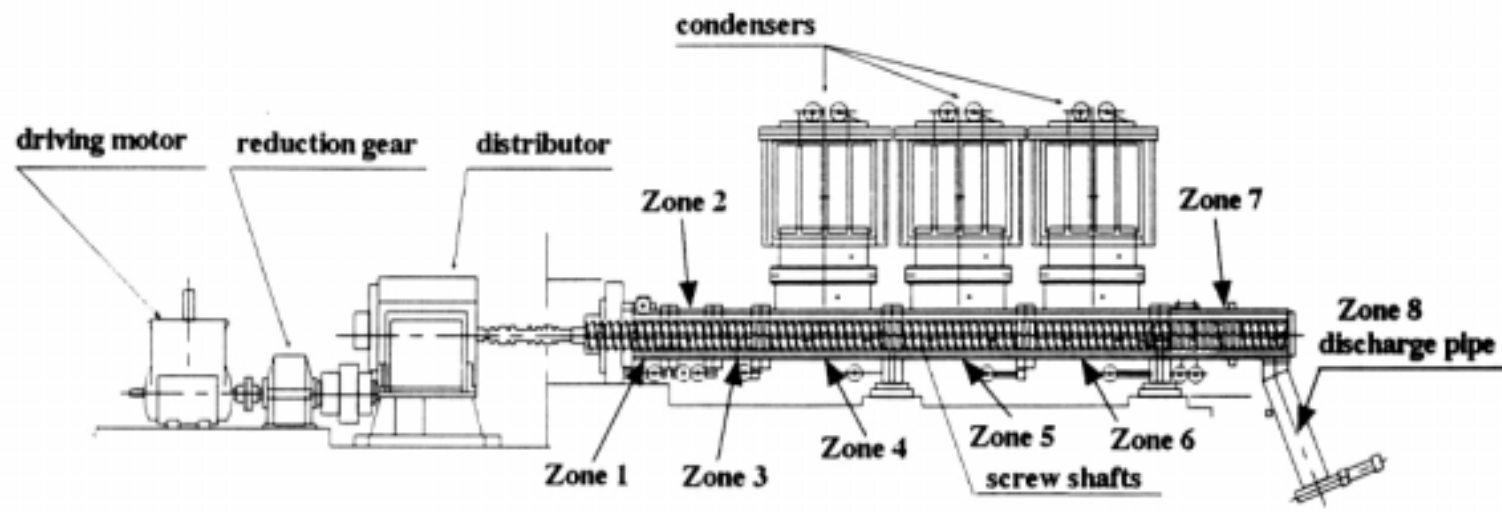


Figure 2. 7 Extruder of bituminization facility in Tokai Works

2. Fire hazards in the nuclear reprocessing facilities

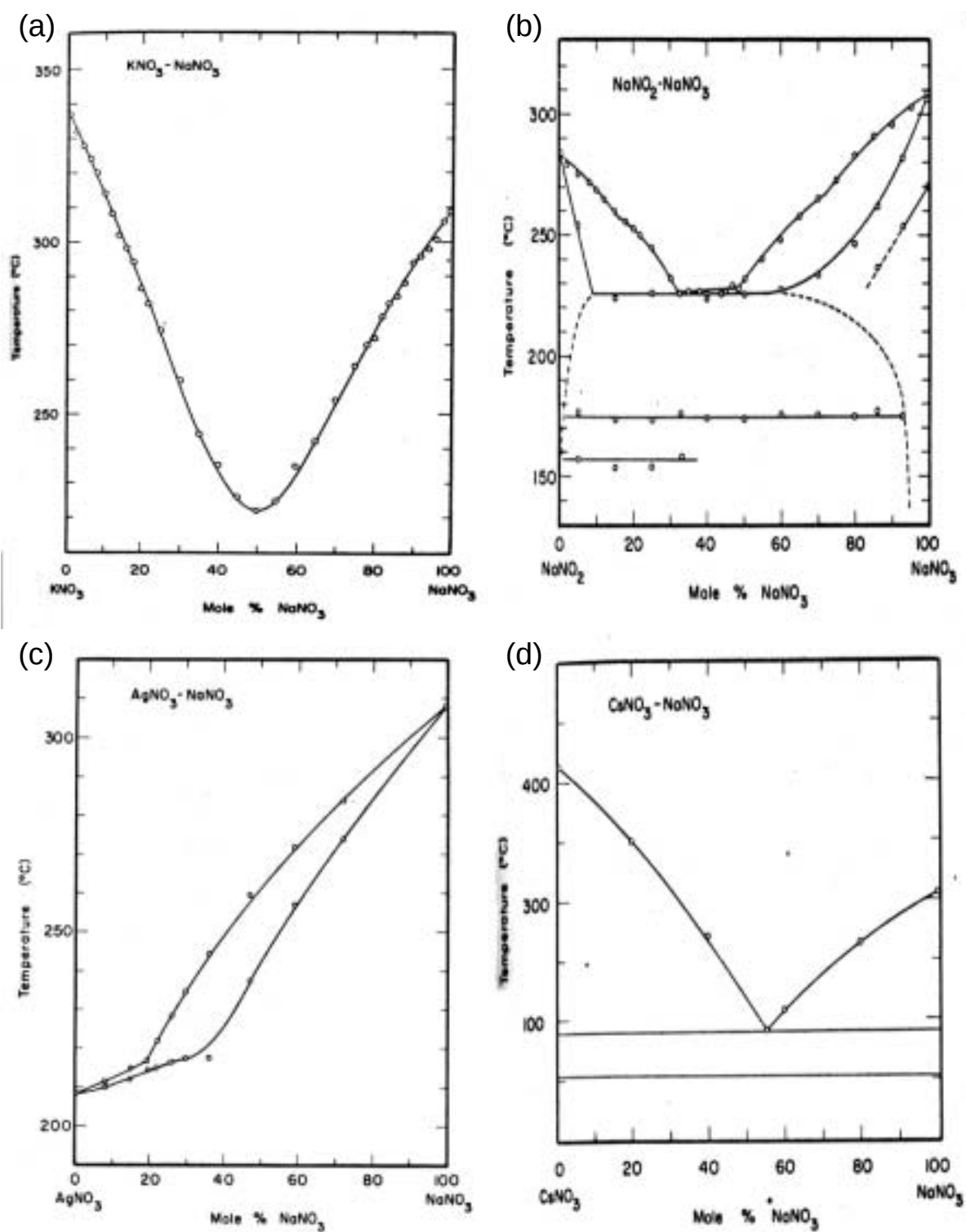


Figure 2.8 Phase diagrams for (a) $\text{KNO}_3 - \text{NaNO}_3$, (b) $\text{NaNO}_2 - \text{NaNO}_3$, (c) $\text{AgNO}_3 - \text{NaNO}_3$ and (d) $\text{CsNO}_3 - \text{NaNO}_3$ [8]

2. Fire hazards in the nuclear reprocessing facilities

References

- [1]. Pamela L. Gordon, Charles O'Dell and John G. Watkin, Investigation of red oil decomposition by simulated Hanford tank wastes, *J. Hazard. Mat.*, 39 (1994) 69-86.
- [2]. S.A. Kabakchi, A.V. Putilov and E.R. Nazin, Analysis of data and physicochemical modeling of the radiation accident in the southern urals in 1957, *Atomic Energy*, 78(1) (1995) 44-47.
- [3]. D.T. Hobbs, Possible Explosive Compounds In The Savannah River Site Waste Tank Farm Facilities, DOE Report, (1991) WSRC-TR-91-444.
- [4]. H. Babad, R.J. Cash, J.L. Deichman and G.D. Johnson, High-priority Hanford Site radioactive waste storage tank safety issues: An overview, *J. Hazard. Mat.*, 35 (1993) 427-441.
- [5]. L.W. Gray, An explosion and fire during conversion of liquid uranyl nitrate to solid uranium oxide, *Nuclear Safety*, 19(1) (1978) 91-99.
- [6]. M.L. Hyder, W.G. Lussie and F.E. Witmer, Explosion in the Tomsk-7 reprocessing plant on april 6, 1993, *Nuclear Safety*, 37(3) (1996) 222-234.
- [7]. D.F. Paddleford and H.K. Fauske, Safe venting of "Red oil" runaway reactions, *National Heat Transfer Conference*, (1995) 193-200.
- [8]. G.J. Janz, Ursula Krebs, H.F. Siegenthaler and R.P.T. Tomkins, Electrical Conductance, Density, Viscosity, and Surface Tension Data, *J. Phys. Chem. Ref. Data*, 1(3) (1972) 621, 667, 681, 741.
- [9]. Roy E. Gephart and Regina E. Lundgren, Hanford Tank Cleanup: A guide to Understanding the Technical Issues, Battelle Press, Ohio, 1995.
- [10]. B.A. Crawford, R.S. Addleman, T.V. Rebagay, G.L. Troyer, S.J. Mech and F.R. Reich, An Approach to Molecular Characterization of Hanford Site Waste Tanks, DOE report, (1992) WHC-SA-1540.
- [11]. J.A. Cambell, R.W. Stromatt, M.R. Smith, D.W. Koppenaal, R.M. Bean, T.E. Jones, D.M. Strachan and H. Babad, Organic Analysis at the Hanford, *Anal. Chem.*, 66 (1994) 24.
- [12]. Zh. Medvedev, The decades of dissidence, *New Scientist*, 72 (1976) 264.
- [13]. Zh. Medvedev, Facts behind the soviet nuclear disaster, *New Scientist*, 73 (1977) 761.
- [14]. J.H. Fremlin, Nuclear detective story, *Nature*, 282(8) (1979) 157.

2. Fire hazards in the nuclear reprocessing facilities

- [15]. W. Stratton, D.Stillman, S.Barr and H. Agnew, Are Portions of the Urals Really Contaminated?, Science, 206 (1979) 423-425.
- [16]. Theodore A. Postol, The Incident in Chelyabinsk, Science, 206 (1979) 326-327.
- [17]. John R. Trabalka, L. Dean Eyman and Stanley I. Auerbach, Analysis of the 1957-1958 Soviet Nuclear Accident, Science, 209(4454) (1980) 345-353.
- [18]. M.I. Avramenko, A.N. Averin, E.G. Drozhko, V.P. Filin, Y.V. Glagolenko, E.S. Kotov, B.G. Loboiko, Y.G. Mokrov and G.N. Romanov, Accident of 1957 and Eastern-Urals Radioactive Trace, Report #1 on ISTC Project #48, 1995.
- [19]. N.J. James and G.T. Sheppard, Red oil hazards in nuclear fuel reprocessing, Nuclear Engineering and Design, 130 (1991) 59-69.
- [20]. M.L. Hyder, The reaction of Tri-n-butyl phosphate with nitrates, Nuclear Technol., 116 (1996) 327-333.
- [21]. H.G. Fisher, DIERS Research Program on Emergency Relief Systems, Chem. Eng. Prog., 81(8) (1985) 33-36.
- [22]. H.K. Fauske, New Experimental Technique For Characterizing Runaway Chemical Reactions, Chem. Eng. Prog., 81(8) (1985) 39-46.
- [23]. H.K. Fauske, Emergency Relief System (ERS) Design, Chem. Eng. Prog., 81(8) (1985) 53-56.
- [24]. M.A. Grolmes and J.C. Leung, Code Method for Evaluating Integrated Relief Phenomena, Chem. Eng. Prog., 81(8) (1985) 47-52.
- [25]. M.A. Grolmes, J.C. Leung and H.K. Fauske, Large-Scale Experimentas Of Emergency Relief Systems, Chem. Eng. Prog., 81(8) (1985) 57-62.
- [26]. M.J. Creed and H.K. Fauske, AnEasy, Inexpensive Approach to the DIERS Procedure, Chem. Eng. Prog., 86 (March 1990) 45-49.
- [27]. H.K. Fauske, Emergency relief system design for runaway chemical reaction: extension of the diers methology, Chem. Eng. Res. Des., 67 (March 1989) 199-202.
- [28]. R.M. Wallace, Ammonium Nitrate in the Vessel Vent system, USDOE Report, DPST-76-421 (November 10, 1976) E.I. du Pont de Nemours and Co..
- [29]. N. Sasaki, T. Koyama, E. Omori, A. Maki and T. Yamanouchi, Study on the Cause of the Fire and Explosion Incident at Bituminization Demonstration Facility of PNC Tokai Works, SPECTRUM'98, III (1998) 67-77.
- [30]. Yasuhito Igarashi, Michio Aoyama, Takashi Miyao, Katsumi Hirose, Kazuhisa Komura

2. Fire hazards in the nuclear reprocessing facilities

and Masayoshi Yamamoto, Air concentration of radiocaesium in Tsukuba, Japan following the release from the Tokai waste treatment plant: comparisons of observations with predictions, *Applied Radiation and Isotopes*, 50 (1999) 1063-1073.

[31]. Incident Investigation Committee, About the fire and explosion incident at the Bituminization Demonstration Facility of PNC Tokai Works (in Japanese), (Dec 15, 1997)

[32]. T. Koyama, A. Shibata, Y. Sano, E.. Omori, H. Suzuki, Y. Kato, F. Kitatani, K. Kosugi, N. Kikuchi, T. Sudo, T. Shimizu, H. Fujita, A. Maki and T. Yamanouchi, The Fire and Explosion Incident at Bituminization Demonstration Facility of PNC Tokai Works (in Japanese), *J. of the Atomic Society of Japan*, 40(10) (1998) 740-766.

[33]. M. Demonie , E. Detilleux , H. Eschrich , W. Hild , A. Osipenco and R. Reynders, The fire incident in the eurobitum plant on december 15, 1981 : Description, Evaluation and Conclusions, Eurochemic, Belgium, December 1990.

[34]. Kazutoshi Hasegawa and Yongfu Li, Explosion of Asphalt-Salt Mixtures in a reprocessing plant, *AiChE Spring National Meeting, Nuclear Engineering Group #14*, (1999)

[35]. Yongfu Li and Kazutoshi Hasegawa, Study on the cause of the fire and explosion accident in Tokai Bituminization Facility(V) (in Japanese), *Academic Society of Safety Engineering*, (July 1999)

3.Experimental apparatus

3.1. Evaluation methods of the hazardous chemical reactions

One of the hazards of the most concern in the chemical industry is the thermal hazard, which is governed by the thermodynamics and chemical kinetics of usually complex chemical reactions taking place in the chemical system. There are a lot of evaluation methods of hazardous chemical reactions. They include the spontaneous ignitability test, the Koenen test, the pressure vessel test, adiabatic storage test, the isothermal test, the self-heating decomposition temperature test (SADT) [1] and 75°C stability test. In the past, techniques such as differential scanning calorimetry (DSC) [2] and differential thermal analysis (DTA) were the primary methods used in hazard analysis.

Thermodynamic data, kinetic parameters and physical properties of the reactants together with the reactor condition are required for assessing runaway reaction hazards. These data can be obtained by DSC, accelerating rate calorimetry (ARC)[3], and recently by reaction calorimetry (RC) [4]. Emergency relief venting due to runaway reaction has extensively been studied by DIERS[5] (Design Institute of Emergency Relief System) of AIChE. Some theoretical models and criteria have been developed for predicting the critical conditions that may lead to runaway based on heat releasing rate and heat transfer characteristics of the process vessel.

In the present work, evaluation of single elements was done by conventional TG-DTA. A study of the reactive chemical hazard between bitumen / nitrate was conducted by a specially arranged device for this work which was larger than the commercially available ARC equipment. Adiabatic conditions were maintained in the ARC provided that the rate of temperature increase did not exceed about $10^{\circ}\text{C min}^{-1}$. In this work, the heating rate ranged from 0.5 to $4^{\circ}\text{C min}^{-1}$.

3.2. Thermal gravimetric-differential thermal analysis (TG-DTA)

3.2.1. The principles of apparatus

The endothermic/exothermic behavior of the transformation, melting and reaction of the sample can be measured by DTA. The principles of the DTA are shown on Figure 3.1. The furnace was heated at constant rate (dT_p/dt). The temperature of furnace, reference and sample, T_p , T_R and T_S , respectively are shown in relation to the elapsed time in Fig. 3.1. T_R and T_S increase at constant rate of dT_p/dt after the relaxation time. The following equation comes into existence at the steady state.

$$dT_p/dt = dT_R/dt = dT_S/dt \quad (1)$$

In the steady state, T_p minus T_S is equal to constant. Yielding from the Newton's law of cooling, the heat flux (dq_s/dt) is defined as follows:

$$dq_s/dt = (T_p - T_S) / R \quad (2)$$

This equation means that the heat flux is proportional to the temperature difference between furnace and sample and this proportional constant equals the inverse of the heat resistance constant (R). This value is dependent on the furnace and the cell, which means that this value belongs to the apparatus coefficient. Observing the relation of the thermal valance ($\Delta q = C_p \Delta T$) the heat flux to the sample (dq_s/dt) at the steady state is given by:

$$dq_s/dt = (C_{C(S)} + C_S) dT_p/dt \quad (3)$$

$C_{C(S)}$: Thermal Capacity of sample cell

C_S : Thermal Capacity of sample

Combination of Eq.(2) and Eq.(3) gives

$$dq_R/dt = (T_p - T_R) / R = (C_{C(R)} + C_R) dT_p/dt \quad (4)$$

$C_{C(R)}$: Thermal Capacity of reference cell

C_R : Thermal Capacity of reference

Combination of Eqs. (3) and (4) yields Eq.(5)

$$\begin{aligned} dq_s/dt - dq_R/dt &= d\Delta q/dt \\ &= -(T_S - T_R) / R = -\Delta T / R \\ &= \{(C_{C(S)} - C_{C(R)}) + (C_S - C_R)\} dT_p/dt \end{aligned} \quad (5)$$

The heat capacity and weight of the sample are the same with these of the reference cell. We define the heat capacity of the reference cell is equal to zero ($C_R=0$). The following equation is obtained which only depends on the C_S .

$$d\Delta q/dt = -\Delta T / R = C_S dT_P/dt \quad (6)$$

From Fig. 3.1, the relation between the temperature difference (ΔT) and thermo electromotive force (ΔE) is expressed by

$$\Delta E = S_{AB}\Delta T \quad (7)$$

S_{AB} : the thermoelectric power difference between thermocouple A and B

From Eqs.(6) and Eq.(7), the following equation is obtained.

$$d\Delta q/dt = -\Delta E / R / S_{AB} \quad (8)$$

3.2.2. TG-DTA analysis

Molecular distribution of bitumen is shown in Fig.3.2. The average molecular weight (MW) was estimated at 1260 using the ebullioscopic method. From this result the chemical structure of bitumen was assumed as given in Fig. 3.3. Basically the bitumen is composed of heterocyclic compounds. Generally, there are two types of asphalts in the petroleum asphalts produced by distillation of petroleum: straight asphalt and blown asphalt. The former is produced as the distillation residue of crude oil and the latter is produced by oxidizing the straight asphalt by air blowing. In the low-level waste bituminization in power plants, the straight asphalt is used, while, in the reprocessing bituminization of PNC, a compound asphalt is used, which was produced by mixing the straight and blown asphalt. This type of compound asphalt was produced by the order of PNC and is not commercially available at present. Therefore, commercially available blown asphalt is used in the present work. Asphalt is also called bitumen. The term bitumen is used to express asphalt in the present work.

Prior to the study of self-ignition temperature of bitumen, the exothermic/endothermic behavior was investigated by means of thermal gravimetric-differential thermal analysis (TG-DTA). The tested chemical reagents and materials are commercially available blown bitumen asphalt 20/30 (Showa SHELL Corp.), PNC-type AD Compound Bitumen (kindly supplied by PNC), NaNO_3 , AgNO_3 , $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$ and $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. The sample was heated from room temperature to 500 °C in air atmosphere. The heating rate was 2°C/min. The powdered Al_2O_3 was used as the standard sample. The weights of the samples were in the range of 6.89 to 19.58 mg.

3.2.3. Experimental results

Thermal stabilities of two types of bitumen, commercial bitumen 20/30 and PNC AD compound Asphalt (PNC-type bitumen) were analyzed by TG-DTA upto 500°C. The results are shown in Fig. 3.4. Gradual heating was observed from the room temperature to approximately 350 °C, and then weight loss started above 350 °C. The heat flow instability above 350°C is considered to be coupled with decomposition or evaporation of light components in the bitumen. A largely exothermic reaction was observed in the range from 425 to 500°C in each bitumen sample. It is confirmed that the pattern of the thermal stability is very similar to each other and both the bitumens are stable up to 340 °C.

The TG-DTA analyses for four salts are shown in Figure 3.5(a-d). It is clearly seen that NaNO₃ is thermally stable up to 500°C. While other tested salts are decomposed or oxidized at lower temperature, AgNO₃ is decomposed above 350°C to AgO releasing NO₂ as



Figure 3.5(c) indicates that the crystallized water molecules of K₄Fe(CN)₆·3H₂O were released under 100 °C. The thermal reaction observed in DTA and the increase in weight above 300 °C are attributed to the oxidation of Fe(II) ions under air atmosphere.

Ni(NO₃)₂·6H₂O is very hygroscopic. Figure 3.5(d) suggests that dehydration of additive associating water molecule was initiated under 100°C. The catalyzed water molecules were released in the range from 100 to 200 °C and finally hydrated Ni(NO₃)₂ was decomposed to NiO + HNO₃ + NO_x above 200 °C as



3.3. Furnace system

3.3.1. Heating apparatus

We have prepared a handmade heating apparatus. To measure the ignition temperature, we chose the following system after try and error experimental study. The sample cooled down to the room temperature was set in the electric furnace of which temperature was controlled by a PID

(proportional integral derivative) controlling power source, ULVAC Thermal Program Controller HPC-5000. Fig. 3.6. shows the temperature measurement system used in the present work. The air bath sample room was a 70-mm diameter steel cylinder with a height of 130 mm. The apparatus was specially designed in the present work. As the sample was explosive material, the amount of the sample should be small as small as possible. However, the balances in the thermal generation radiation, conductance, absorption, etc. are very important. Thus the size of the sample was decided according to the above-mentioned factors.

The environmental temperature was measured at the surface of the sample vessel and the sample temperature was measured inside. To meet this condition, the present size of experimental system was found to be appropriate after try and error experiments. The sample was heated at the constant increase rate of 2.0 °C /min by a heater surrounding the cylindrical sample room, in which the sample beaker was placed, until the ignition took place. The sample room was covered with thermal insulator KAOWOOL(alumina-silica short fiber). After the sample was fired by itself, the furnace was switched off. The self-ignition temperature was read as the initiating point of rapid temperature rise. The ignition was also visually confirmed by the rapid increase in smoking.

3.3.2. Temperature measurement system

The temperatures in the heating apparatus were measured with five CA thermo-couples covered with 316SS tube, 1.6x300 mm. Two of them were set on the outside surface of the sample room to measure the heater temperature. One was placed just above the sample in the sample room to monitor the firing temperature. The rest two were inserted in the sample at different places considering the inhomogeneous temperature distribution in the sample. The thermo-couples were connected to a digital voltmeter, Kethley multimeter 2000, to read the temperatures. All the temperature data were put into a personal computer through an interface. The temperatures were monitored with analog recorders directly connected to the thermo-couple

3. Experimental apparatus

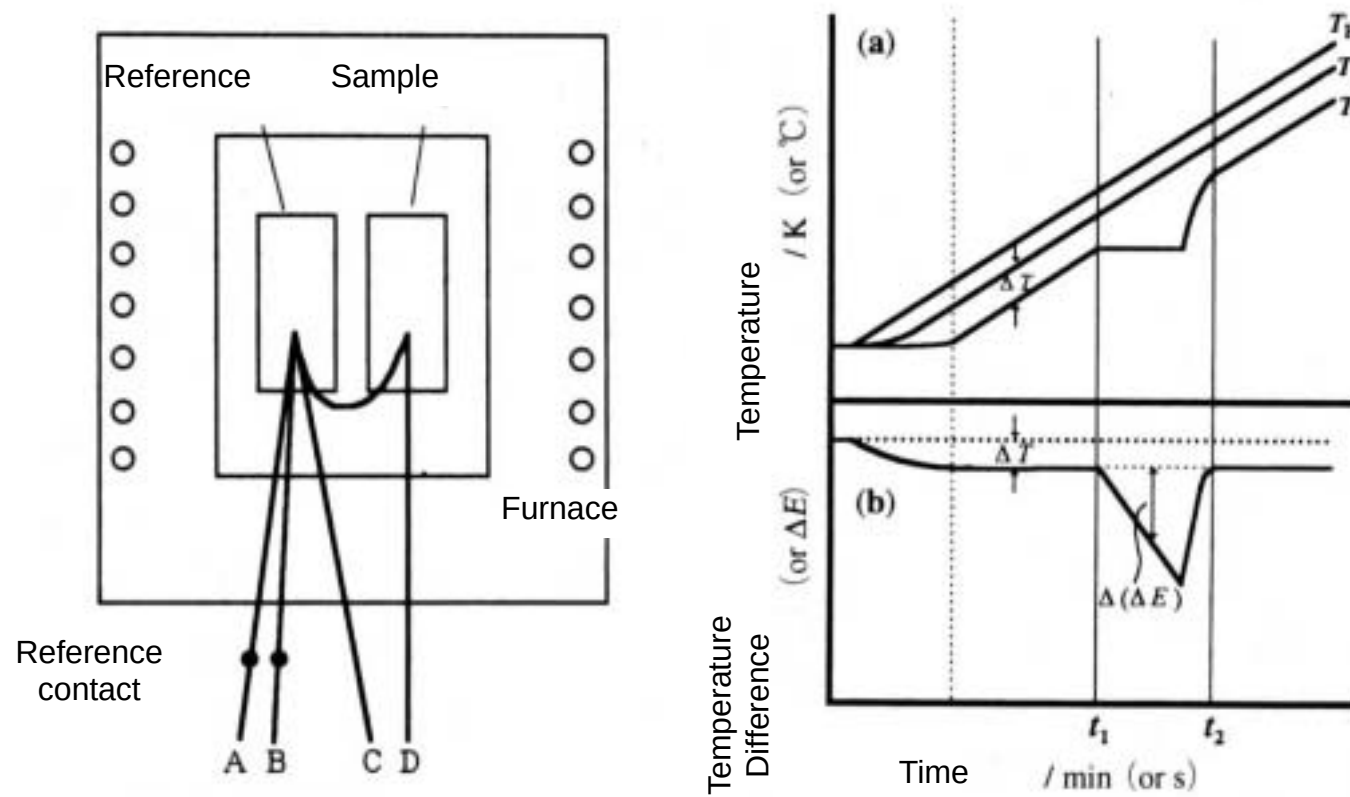


Figure 3. 1

Schematic diagram of constitution and principle of DTA

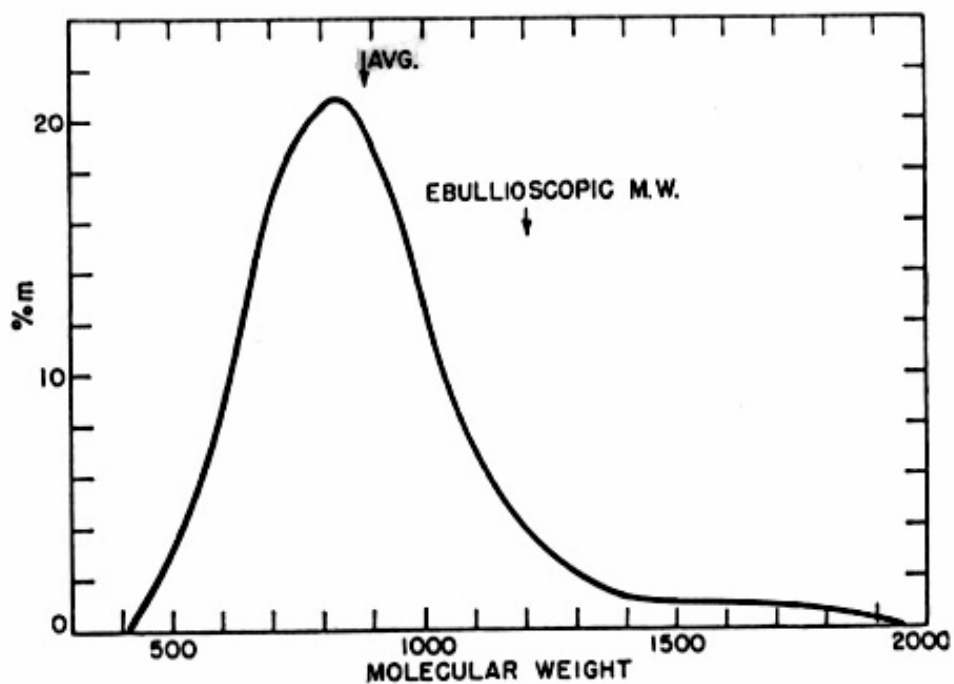


Figure 3. 2 Molecular weight distribution of ASP by the mass spectrometer.

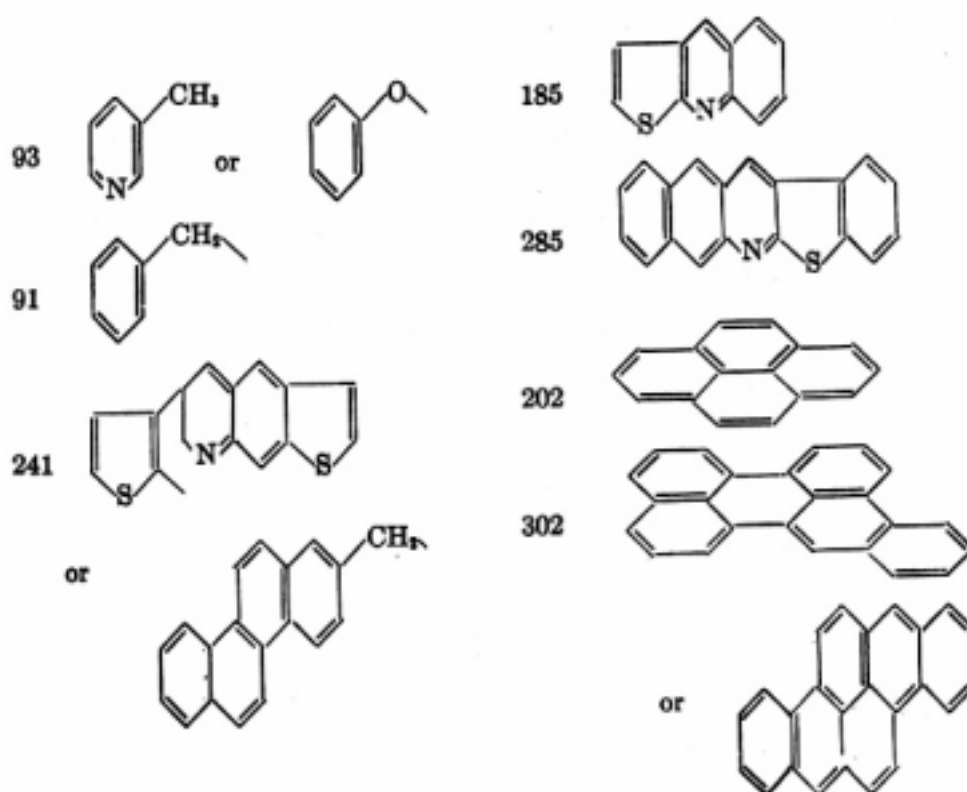


Figure 3. 3 Assignments of fragment peaks in mass spectrum of ASP.

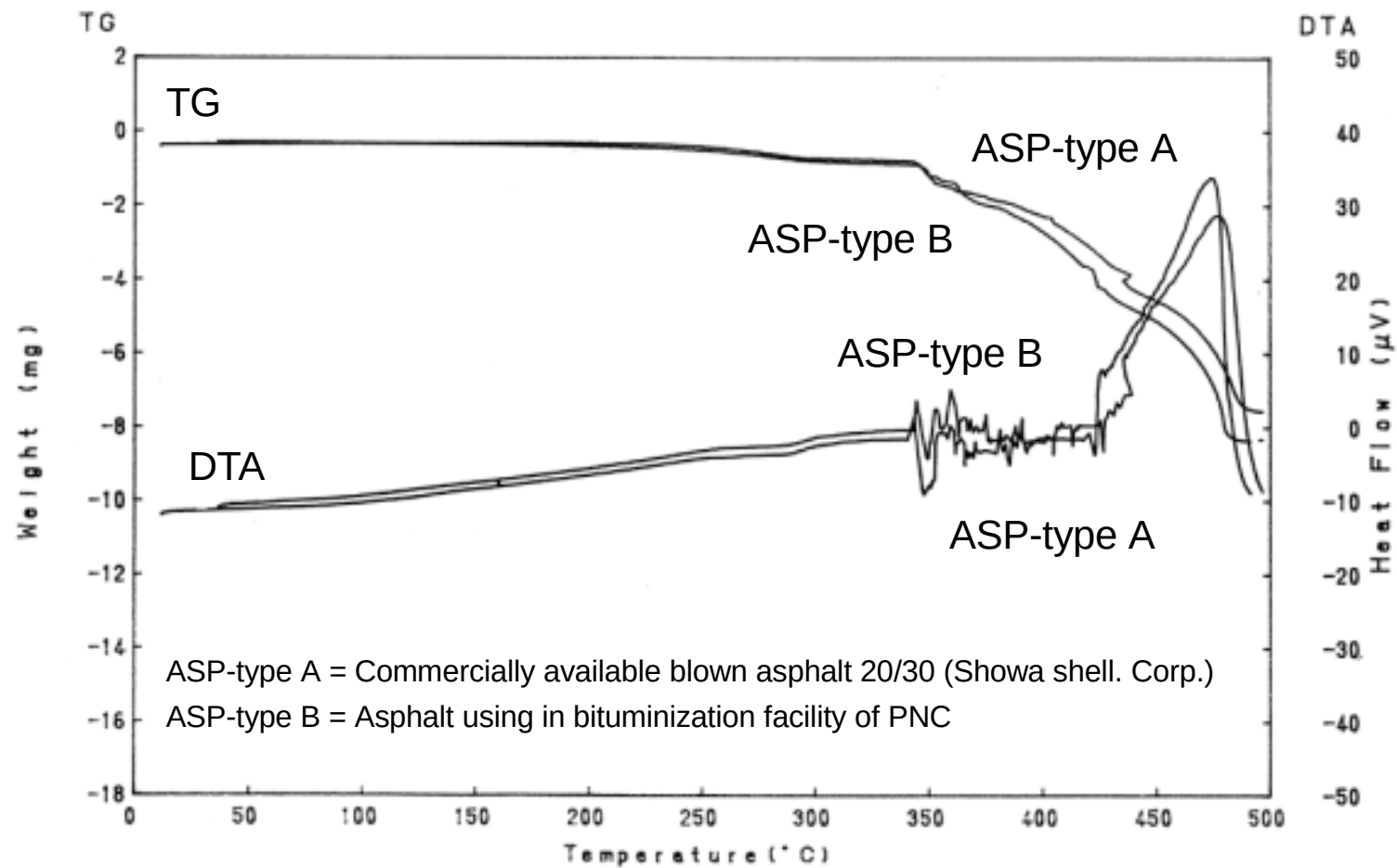


Figure 3. 4 TG-DTA analysis of bitumens.

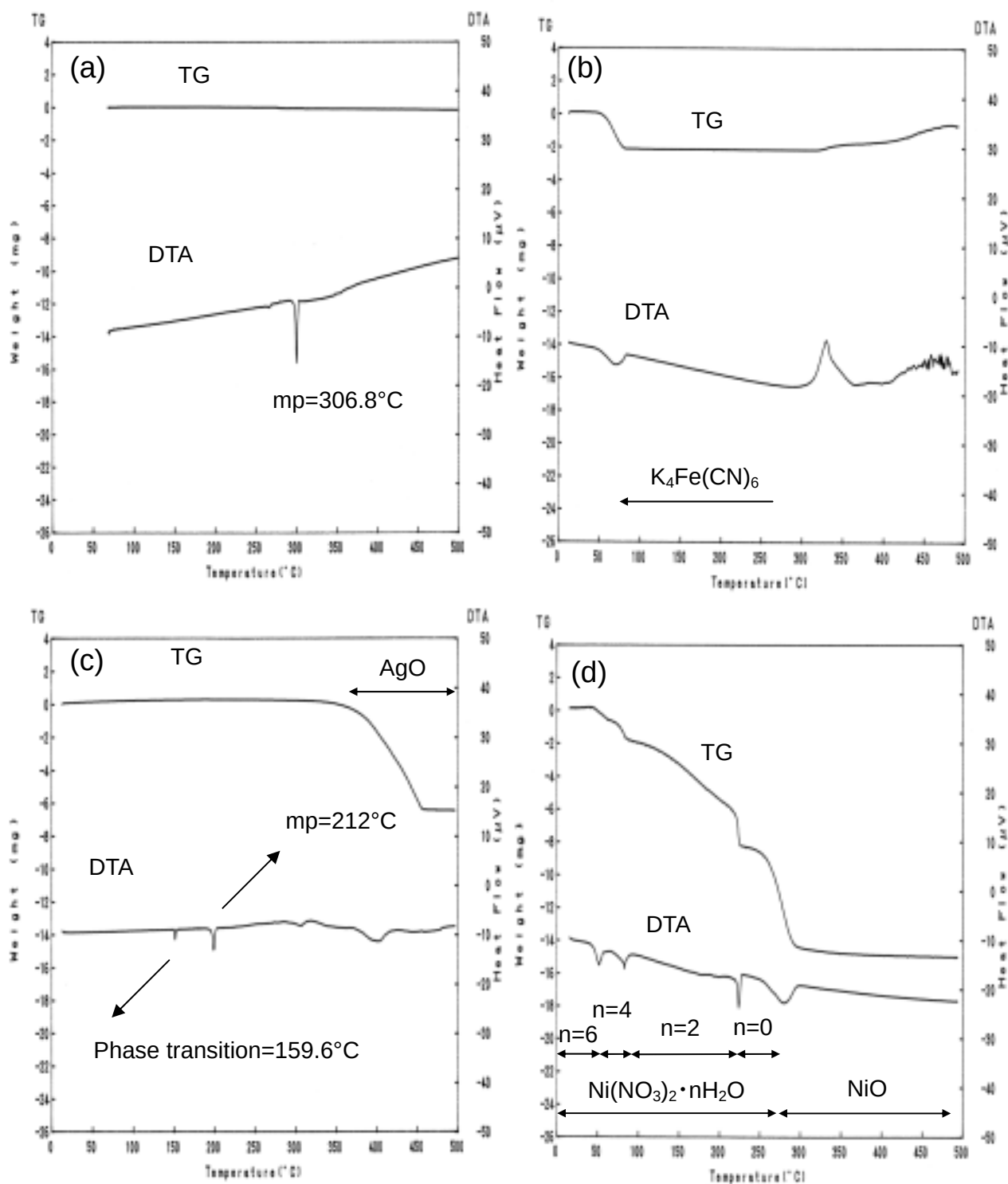


Figure 3.5 TG-DTA curves of NaNO₃ (a) , K₄Fe(CN)₆·3H₂O (b) , AgNO₃ (c) and Ni(NO₃)₂·6H₂O (d) at a heating rate of 2°C/min in Air-flow

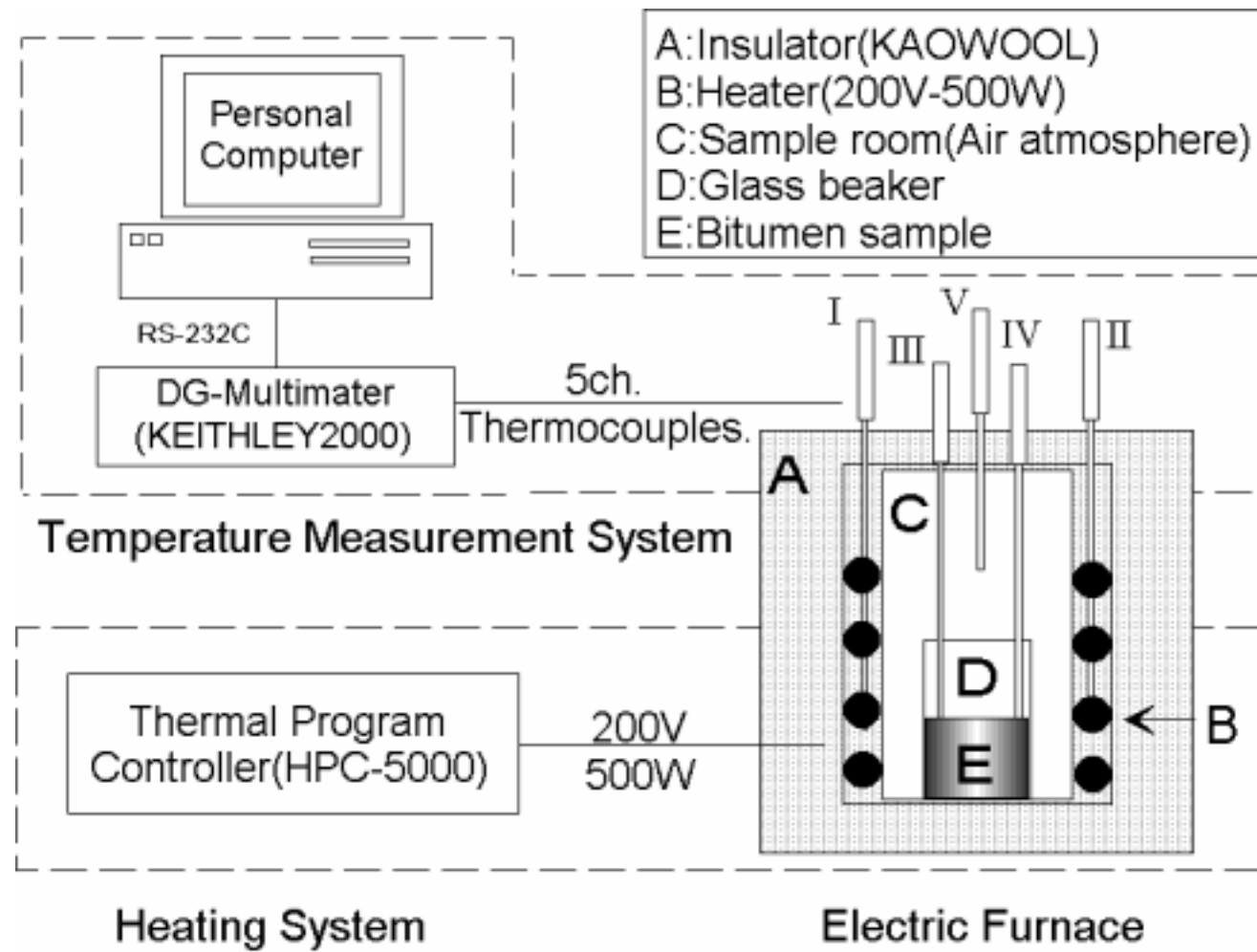


Figure 3. 6 Experimental apparatus of electric furnace

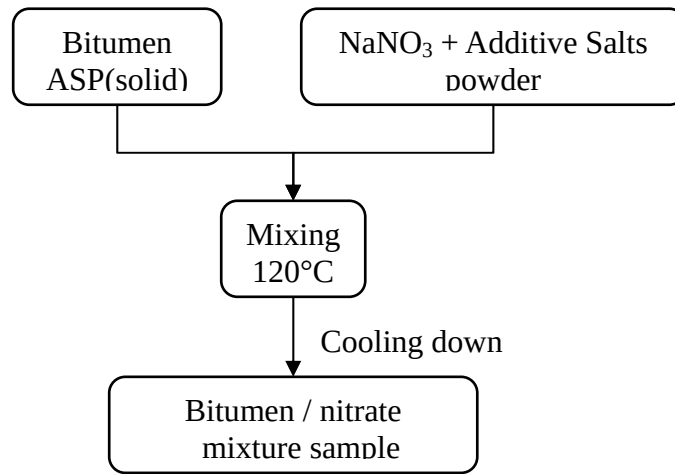


Figure 3. 7 Sample preparation diagram in this work.

References

- [1] D.C. Noller, S.J. Mazourowski, G.F. Linden, F.J.G. de Leeuw and O.L. Mageli, *Ind. Eng. Chem.*, 56(12) (1964) 18.
- [2] T. Ando, Y. Fujimoto and S. Morisaki, Analysis of differential scanning calorimetric data for reactive chemicals, *J. Haz. Mater.* 28 (1991) 251-280.
- [3] D.I. Townsend, Thermal Hazard Evaluation by an Accelerating rate calorimeter, *Thermochim. Acta*, 37 (1980) 1-30.
- [4] YS. Duh, CC. Hsu, CS. Kao and SW. Yu, Application of reaction calorimetry in reaction kinetics and thermal hazard evaluation, *Thermochim. Acta*, 285 (1996) 67-79.
- [5] H.K. Fauske and J.C. Leung, New experimental technique for characterizing runaway chemical reactions, *Chem. Eng. Prog.*, 81(8) (1985) 33-36.

4. The self-ignition temperature of bitumen / nitrate mixture

4.1. Introduction

The chemical reaction involved in the firing mechanism must be very complicated. The information on the chemical reaction relating to the bituminization process (Fig. 4.1) should be acquired as much as possible. The purpose of this section, therefore, is not to identify the direct cause of the accident, but to investigate the chemical reactions which may reach the self-ignition of organic materials containing nitrates salts, by taking the example of the materials dealt with in the bituminization plant of the reprocessing.

On the basis of the above-mentioned viewpoint in the present work, the self-ignition temperatures are studied on the blown bitumen mixed with sodium nitrate and some chemicals which are added in the bituminization process to adjust pH and to immobilize the radioactive isotopes of Cs, Sr and I. In particular, attention is placed to the additive effects of $\text{Ni}(\text{NO}_3)_2$ and AgNO_3 ; The former may exist in the waste stream and the latter is added to the waste to immobilize I.

If $\text{Ni}(\text{NO}_3)_2$ exists in the waste stream, there is a possibility that $\text{Fe}(\text{NO}_3)_3$ also exists in the processed waste stream. $\text{Fe}(\text{NO}_3)_3$ releases NO_x gases at relatively low temperature range of 100-200 °C and Fe(III) itself works as an oxidizing agent against organic materials. The experimental study was extended in the present work to measurement of the viscosity alternation of the bitumen mixture when $\text{Fe}(\text{NO}_3)_3$ is added.

In the PNC plant, the torque of extruder had been monitored as shown in Figure 4.2. Although the absolute value of torque was not shown here, the torque changed cyclically during the normal operation process and the usual deviations of the torque were normally 20-30% except some jumping point. On the other hand, the torque measurement showed

4. The self-Ignition Temperature of bitumen / nitrate mixture

unusual increase and fluctuations in the process of the batches of No. 27-29, which are related to the accident. The oxidation of the bitumen by the air mixed in the extruder was suspected as the reason for the torque increase. However, the oxidation by the air is known to proceed not so fast as shown in the torque measurement. Then the friction of precipitates is another suspected cause for the torque deviation. The torque change was one of the strange facts of the extruder mixing in the process of the accident.

The present work has been initiated by the accident of the PNC plant and it is one of the aims of the present work to accumulate information of chemical reactions which may relate to the reprocessing waste treatment. In particular, the present work deals with the oxidation of bitumen in the presence of $\text{Ni}(\text{NO}_3)_2$, $\text{Fe}(\text{NO}_3)_3$ and AgNO_3 . However, it should be pointed out that to identify the chemical reaction directly relating the accident is out of scope of the present work.

4.2. Experimental

4.2.1. Thermal gravimetric-differential thermal analysis

The experimental methods were stated in Chapter 3 in detail.

4.2.2. Preparation of the samples

In the bituminization process, several reagents were added in the waste solution to immobilize radioactive isotopes and to adjust pH. In the present work, commercially available blown bitumen 20/30 were used to measure the self-ignition temperature (SIT) of the bitumen in the presence of additive salts.

At first in the present work, the samples were prepared by mixing 25 g of the bitumen with 10 g of NaNO_3 and 5 g of additive salt in question. Tested additive salts here are Na_2SO_3 , $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, AgNO_3 , $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$ and $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. Former four reagents were used in the bituminization facility of PNC as the immobilization reagents for radioactive isotopes. The last one $\text{Ni}(\text{NO}_3)_2$ is not used in the facility as the additive reagent, but examined in the present work due to the reason mentioned in section 3.1. In addition $\text{Ni}(\text{NO}_3)_2$ may exist at

4. The self-Ignition Temperature of bitumen / nitrate mixture

low concentration in some exceptional cases where there exists a material imbalance among the reagents of BaOH, HNO₃, NaOH and NiSO₄ added to the waste solution.

By adding the powders of the additive reagents to bitumen at room temperature, the sample was heated to 120°C and stirred at 120°C for ca. 10 min to disperse the powder homogeneously in the sample until the green powder of Ni(NO₃)₂ did not be visibly recognized. To compare the ignition temperature of the sample blown bitumen, the firing temperature of the pure bitumen sample was also measured.

In the second phase, attention was paid to the mixing effects of additives of Ni(NO₃)₂ and AgNO₃. Amounts of the blown bitumen 20/30, NaNO₃ and Ni(NO₃)₂·6H₂O were fixed at 25 g, 10 g, and 5 g, respectively. Here the amount of AgNO₃ in each sample was changed from 0.1 g to 5 g. In the case of addition of 0.1 g AgNO₃, two experiments were made; in one experiment the sample was vigorously stirred at ca. 300 rpm for 10 minutes to completely mix the additive reagents and in the other experiment, AgNO₃ powder was just put into the sample without stirring.

4.2.3. The torque measurement of the bitumen mixture

In order to observe the effect of Fe(NO₃)₃ addition, the torque of the bitumen sample was monitored at a constant rotational speed of a stirrer. Figure 4.3 shows the torque measurement apparatus. The torque meter (Type-YT, HEIDON, Japan) was inserted between the shaft of the stirring blade and the driving motor.

Tested bitumen sample was prepared by mixing 50 g of commercially available blown 20/30 bitumen with 20g of NaNO₃ at about 120 °C. The torque of the bitumen sample was measured under a constant rotational speed. Then, as a first step, 1 g of Fe(NO₃)₃ was added at 120 °C and the torque was monitored at constant rotation of stirring motor for 30 min. As a second step 4 g of Fe(NO₃)₃ was added to the bitumen sample and again the torque was monitored for 60 min.

4.3. Results and Discussion

4.3.1. TG-DTA Analysis

The result indicates that the commercially available blown bitumen 20/30 is usable as a test material for PNC type bitumen of which availability is very limited. TG-DTA analyses on pure reagent of NaNO_3 , AgNO_3 , $\text{Ni(NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{K}_4\text{Fe(CN)}_6 \cdot 3\text{H}_2\text{O}$ were also conducted. It was found that NaNO_3 was thermally stable up to 500 °C, while other tested salts were decomposed or oxidized at lower temperatures. AgNO_3 was decomposed to Ag_2O above 350 °C releasing NO_2 . It is known that the crystallization water molecules of $\text{K}_4\text{Fe(CN)}_6 \cdot 3\text{H}_2\text{O}$ are released under 100 °C. The thermal reaction observed in DTA and the increase in weight above 300 °C are attributed to the oxidation of Fe(II) ions under the air atmosphere.

$\text{Ni(NO}_3)_2 \cdot 6\text{H}_2\text{O}$ is very hygroscopic. Dehydration of the additive associating water molecule was initiated under 100 °C. The crystallized water molecules were released in the range from 100 to 200 °C and finally hydrated $\text{Ni(NO}_3)_2$ was decomposed to $\text{NiO} + \text{HNO}_3 + \text{NO}_x$ above 200 °C. The released NO_x is strong oxidation agents. The results suggest that $\text{Ni(NO}_3)_2$ affects the self-ignition of the bitumen mixture.

4.3.2. Measurement of the SIT

4.3.2.1. Additive salt effects

The tested bitumen samples in the present work included nitrates salts and ignited at certain temperature without ignition source. This situation of firing is defined here as self-ignition. Self-ignition-temperatures (SITs) of the bitumen NaNO_3 mixture and the bitumen NaNO_3 mixture with additives of $\text{K}_4\text{Fe(CN)}_6$, NiSO_4 , AgNO_3 , Na_2SO_3 , $\text{Fe(NO}_3)_2$, NaNO_2 and $\text{Ni(NO}_3)_2$ were measured. Figure 6 plots measured temperatures of the bitumen- NaNO_3 mixture (Figure 4.4(a)), the bitumen- NaNO_3 - $\text{Ni(NO}_3)_2$ mixture (Figure 4.4(b)), the bitumen- AgNO_3 mixture (Figure 4.5(a)) and the bitumen- NaNO_3 - $\text{K}_4\text{Fe(CN)}_6 \cdot 3\text{H}_2\text{O}$ mixture (Figure 4.5(b)) under heating at a rising rate of 2°C/min. SIT is here defined as the point where the sample temperature suddenly jumps up or

4. The self-Ignition Temperature of bitumen / nitrate mixture

initiates a rapid increase at a much faster rate than the heating temperatures, resulting in firing. The experimentally observed results are summarized in Table 4.1.

The results clearly show that the additive reagents decrease SITs of bitumen NaNO_3 mixtures. Among the additive reagents, $\text{Ni}(\text{NO}_3)_2$ is the most effective reagent to decrease SIT. Apparently, however, the observed SITs of additive salts are much higher than 200 °C and it is concluded that single addition of above-mentioned materials would not be so much dangerous.

4.3.2.2. Salt segregation effects

When the additive salts are homogeneously distributed in the bitumen, the salts may affect the ignition temperature as independent salts. If the salts are segregated in the bitumen, different phenomena may occur. For example, among the tested reagents the metals of Ni and Ag are frequently used as catalyzers in various chemical processes. In particular, Ag is regarded as an effective catalyzer for oxidation reaction. It was stated in the previous section that release of NO_x from $\text{Ni}(\text{NO}_3)_2$ was observed. The combination effects of the released NO_x and AgNO_3 should be carefully considered. On the basis of above-mentioned point of view, experiments were conducted to consider the mixed effect of two salts, i.e. $\text{Ni}(\text{NO}_3)_2$ and AgNO_3 on the ignition temperatures of the bitumen mixed with NaNO_3 .

The added quantities of AgNO_3 were varied from 0.1 g to 5 g. Figure 4.6 shows the ignition curves of the bitumen mixed with 10g of NaNO_3 , 5 g of $\text{Ni}(\text{NO}_3)_2$ and 5 g of AgNO_3 . The observed self-ignition at 221 °C of this sample is much lower than the ignition of any single additive salt. To know the more detailed information on the effects of AgNO_3 , in particular the quantify effect of AgNO_3 , the net temperature increase is plotted in Fig. 4.7 where temperature difference $T_{\text{Sample}} - T_{\text{Heater}}$ is plotted against T_{Heater} at a given time. The observed heater temperatures, plotted in Fig. 4.7, include small vibrational unstability generated by the temperature controlling system. For the analysis presented in Fig. 4.7, the observed T_{Heater} is smoothened by a least-square fit curve. It is seen in Fig. 4.7 that the temperature is elevated by 300 °C at the maximum after ignition in the case of the bitumen sample containing 5 g of AgNO_3 . It is also seen that the maximum values of the temperature rise after ignition are decreased to 130 °C and 30 °C with decrease in the amounts of AgNO_3 to 2.5 g and 0.58 g, respectively. The net temperature increase at the ignition is nearly

4. The self-Ignition Temperature of bitumen / nitrate mixture

proportional to the added amount of AgNO_3 . Under the present condition, AgNO_3 is concluded to become the initiator which will lead to the fire.

The determined SIT's of the sample examined are summarized in Fig. 4.8. It should be noted that the bitumen nitrate salts mixture is easily fired at around 220 °C, if two reagents of $\text{Ni}(\text{NO}_3)_2$ (5g) and AgNO_3 (above 0.5g) locally coexist in the bitumen. If not stirred, even 0.1g of AgNO_3 was very active and led to self-ignition at 250 °C. This fact suggests the segregation of 5g of $\text{Ni}(\text{NO}_3)_2$ and crystallization of 0.5g of AgNO_3 may become the trigger of fire in bitumen at the temperature around 220 °C.

As mentioned in earlier section, hydrated $\text{Ni}(\text{NO}_3)_2$ is decomposed to NiO , HNO_3 , NO_x and H_2O around 200 °C. The released HNO_3 vapor is regarded as a reactant with hydrocarbons in the bitumen. The reaction is called nitration. In addition, some Ag compounds may be produced at around 200 °C in the presence of HNO_3 vapor and hydrocarbon. For example, it is known that AgOCN is produced when AgNO_3 is heated with HNO_3 and organic materials such as alcohol [2]. If AgCNO and similar compounds were generated, they would react as the trigger of the firing in the bitumen mixture. Similar compound of HgCNO is a very popular ignition material for explosives. PbCNO was reported as firing material generated in the waste treatment by B.Mishra *et al.* [3]. Attention should be paid on the mixing of Ag compound with nitrate salts and organic materials.

4.3.2.3. Torque Measurement of Bitumen Mixture

The relationship between oxidation and viscosity was described by Herrington[4]. He found that the viscosity increase is in proportional to the oxidation rate. In the present experimental process, NO_x is released and $\text{Fe}(\text{NO}_3)_3$ is convert to $\alpha\text{-Fe}_2\text{O}_3$. Both NO_x and Fe_2O_3 are oxidizing agents. Cabanas *et al.* [5] reported that structural phase and homogeneity of iron oxides can be controlled by surrounding atmosphere. In this process Fe^{3+} is reduced to Fe^{2+} by absorbing one electron, and it is noted that bitumen is easily oxidized in the presence of Fe^{3+} ions.

Every nitrate salt becomes an oxidizing reagent when decomposed. For example, NaNO_3 , the major component of the nitrate salts, decomposes at higher temperature than 500 °C. Therefore it is stable in the operational temperature range of bitumen process. As mentioned in earlier section $\text{Ni}(\text{NO}_3)_2$ is decomposed at around 200 °C. In addition, $\text{Fe}(\text{NO}_3)_3$ is known to decompose and release NO_x gases at lower temperatures between 100-200 °C.

4. The self-Ignition Temperature of bitumen / nitrate mixture

Although the SIT of the $\text{Fe}(\text{NO}_3)_3$ is higher than that of $\text{Ni}(\text{NO}_3)_2$, as given in table 1, the behavior of $\text{Fe}(\text{NO}_3)_3$ in bituminization was one of the factors to which attention should be paid. Zeger *et al.*[6] studied the decomposition of $\text{Fe}(\text{NO}_3)_3$ mixed with bitumen in the temperature range from 25°C to 500°C and reported that $\text{Fe}(\text{NO}_3)_3$ decomposes above 100 °C.

Decomposition of $\text{Fe}(\text{NO}_3)_3$ or release of NO_x takes place above 100 °C. The released NO_x gases and Fe^{3+} ions themselves are oxidizing agents and the effects of decomposition should be evaluated even at much lower temperature than the self-ignition temperature of 376°C. From the above mentioned viewpoint, in the present work oxidation by $\text{Fe}(\text{NO}_3)_3$ was studied by torque measurement.

The torque depends on the rotational speed and stirrer shape in addition to the viscosity of the sample. To observe the viscosity change the rotational speed was maintained constant using the same stirrer. Thus the observed value of the torque in Fig. 4.9 shows the relative variation in the viscosity of the bitumen mixture containing $\text{Fe}(\text{NO}_3)_3$. Before the addition of $\text{Fe}(\text{NO}_3)_3$, the torque indicated 0.01 N·m. After addition of 1 g $\text{Fe}(\text{NO}_3)_3$, torque was increased to the maximum value of 0.015 N·m in three minutes. On the other hand after adding 4 g of $\text{Fe}(\text{NO}_3)_3$, the torque was increased to the maximum value of 0.05 N·m in three minutes. Without addition of $\text{Fe}(\text{NO}_3)_3$ the torque of the stirrer was maintained constant at 0.01 N·m for 90 minutes.

In the present experiment, the deviation or the increase in the torque is informative rather than the absolute value of the measured torque. A crude correlation is seen between the maximum increment of torque and the added amount of $\text{Fe}(\text{NO}_3)_3$. Furthermore the reaction time up to the maximum value of the torque, i.e., 3 min on addition of 1g $\text{Fe}(\text{NO}_3)_3$ and 13 min on addition of 4g, is also approximately proportional to the amount of the added $\text{Fe}(\text{NO}_3)_3$. This suggests that the decomposition effect of $\text{Fe}(\text{NO}_3)_3$ is nearly proportional to the amount of $\text{Fe}(\text{NO}_3)_3$. These observations also suggest that the oxidation of bitumen very quickly proceeds.

After the addition of the $\text{Fe}(\text{NO}_3)_3$ it was seen that the torque is initially increased and then decreased. Thereafter the torque became unstable in the case of addition of 4 g $\text{Fe}(\text{NO}_3)_3$, where the torque value is frequently changed. When the bitumen sample is oxidized, the oxidized product increases the viscosity at first but may be dissolved in the surrounding bitumen by stirring. When the amount of oxidized product exceeds a certain limit, some oxidized products could not be homogeneously dissolved and would locally exist. Such a

condition may locally change the viscosity and gives the fluctuation of torque in the rotation of the stirrer on addition of 4 g $\text{Fe}(\text{NO}_3)_3$, as seen in Figure 4.9. From the results of the present work, it is pointed out that monitoring of NO_x gases is important to know the decomposition of $\text{Fe}(\text{NO}_3)_3$ in the bituminization plant, if some nitrate salts of transition elements possibly exist in the process waste stream.

The present work is related to the bituminization of the waste from reprocessing plant. However, the experimental conditions were not completely the same as the operational conditions of PNC plant. Therefore, the present paper does not necessarily conclude the cause of the firing in the PNC plant. In addition, it should be pointed out that the bituminization of nitrate salts is specific to the reprocessing plant and the discussion in the present work is not applicable to the bituminization of LLW in LWRs

4.4. Conclusion

In conclusion, every reagent tested here has decreasing effects on SIT to some extent, although the extent is not so large as to reach the fire. However, $\text{Ni}(\text{NO}_3)_2$ shows a relatively large SIT decrease effect, and furthermore, the mixture of $\text{Ni}(\text{NO}_3)_2$ and AgNO_3 greatly lowers the SIT of blown bitumen. Segregation of these nitrates should be avoided in the bituminization process. It is suggested that, in general, care should be taken in handling Ag in PUREX reprocessing, where nitrate and organic materials coexist in the waste treatment. It is also demonstrated that bitumen is easily oxidized and its viscosity is increased in the presence of $\text{Fe}(\text{NO}_3)_3$. It is suggested that organic materials should not be used as the medium for nitrate waste treatment.

4. The self-Ignition Temperature of bitumen / nitrate mixture

Table 4. 1 Ignition temperature of bitumen mixture with additive salts.

Additive Reagents		SIT / °C
ASP-type A ^{*1}		NSI ^{*2}
Mixture ^{*3}		444
Mixture	+K ₄ Fe(CN) ₆ ·3H ₂ O	399
Mixture	+NiSO ₄ ·6H ₂ O	398
Mixture	+AgNO ₃	395
Mixture	+Na ₂ SO ₃	391
Mixture	+Fe(NO ₃) ₃ ·9H ₂ O	376
Mixture	+NaNO ₂	348
Mixture	+Ni(NO ₃) ₂ ·6H ₂ O	337

*1 ASP-type A = Commercially available Blown Asphalt 20/30 (Showa.Shell Corp.)

*2 No self ignition up to 450 °C

*3 Mixture = ASP-type A(25g) + NaNO₃(10g)

4. The self-Ignition Temperature of bitumen / nitrate mixture

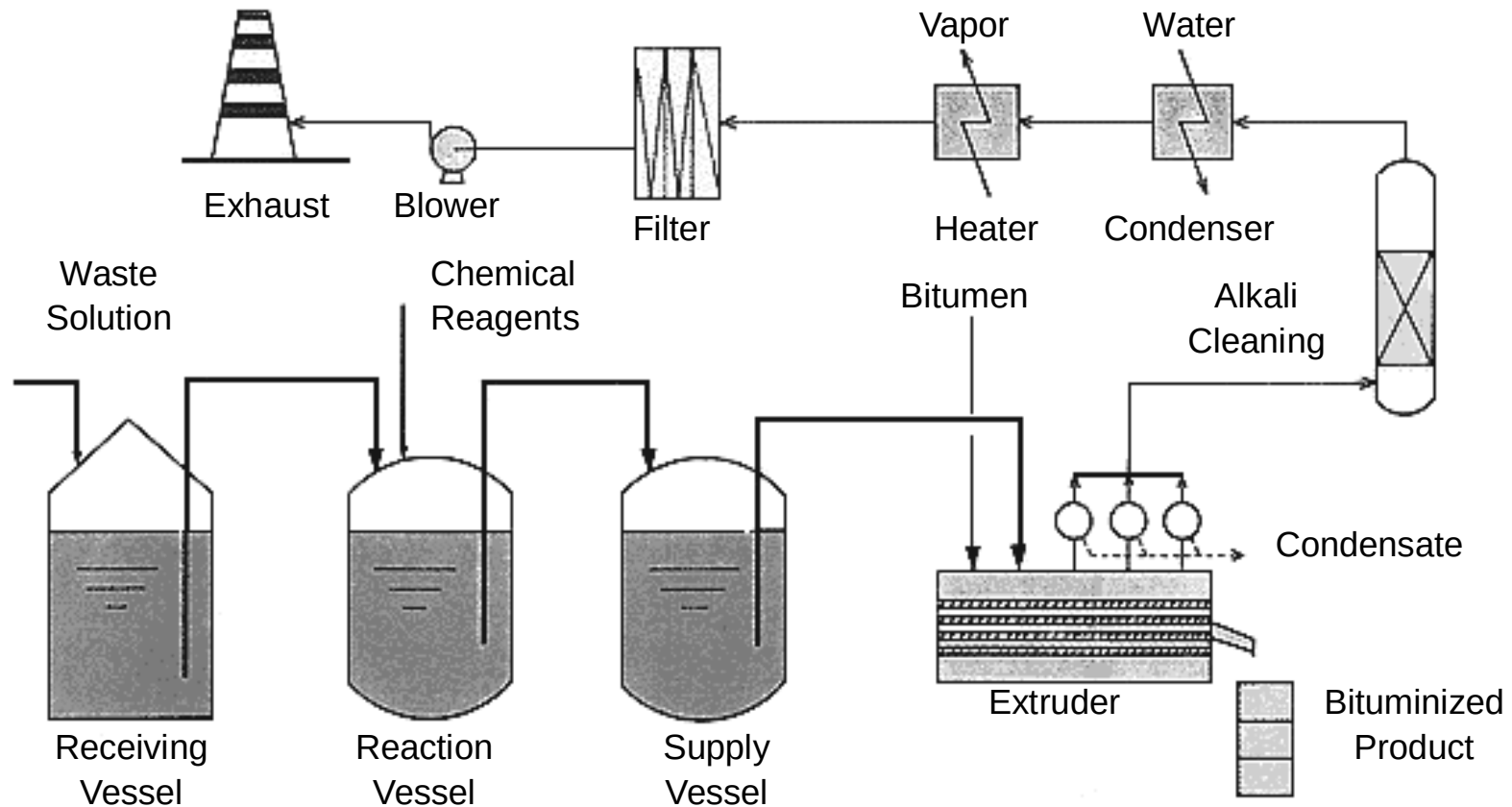


Figure 4. 1 Bituminization facility of PNC.

4. The self-Ignition Temperature of bitumen / nitrate mixture

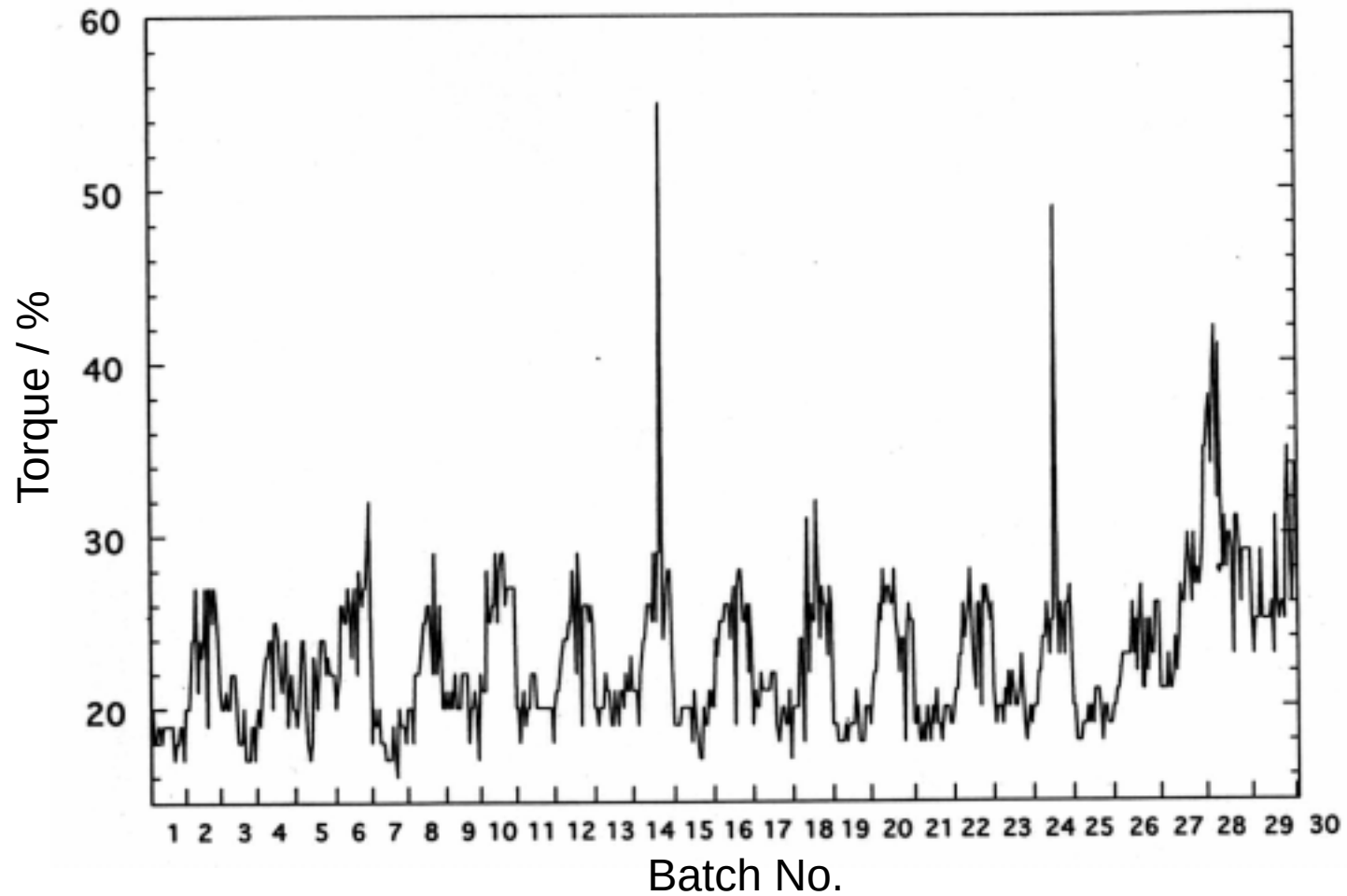


Figure 4. 2 Torque measurement of the extruder in PNC bituminization process

4. The self-Ignition Temperature of bitumen / nitrate mixture

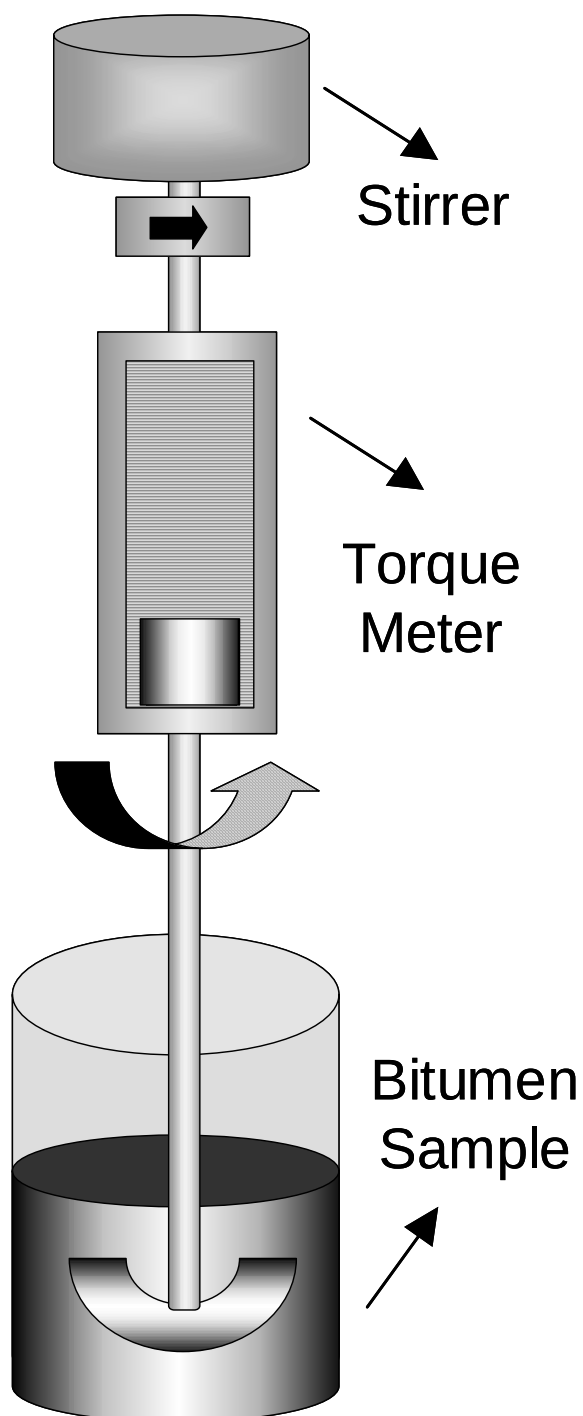


Figure 4. 3 Experimental apparatus of torque measurement of bitumen sample

4. The self-Ignition Temperature of bitumen / nitrate mixture

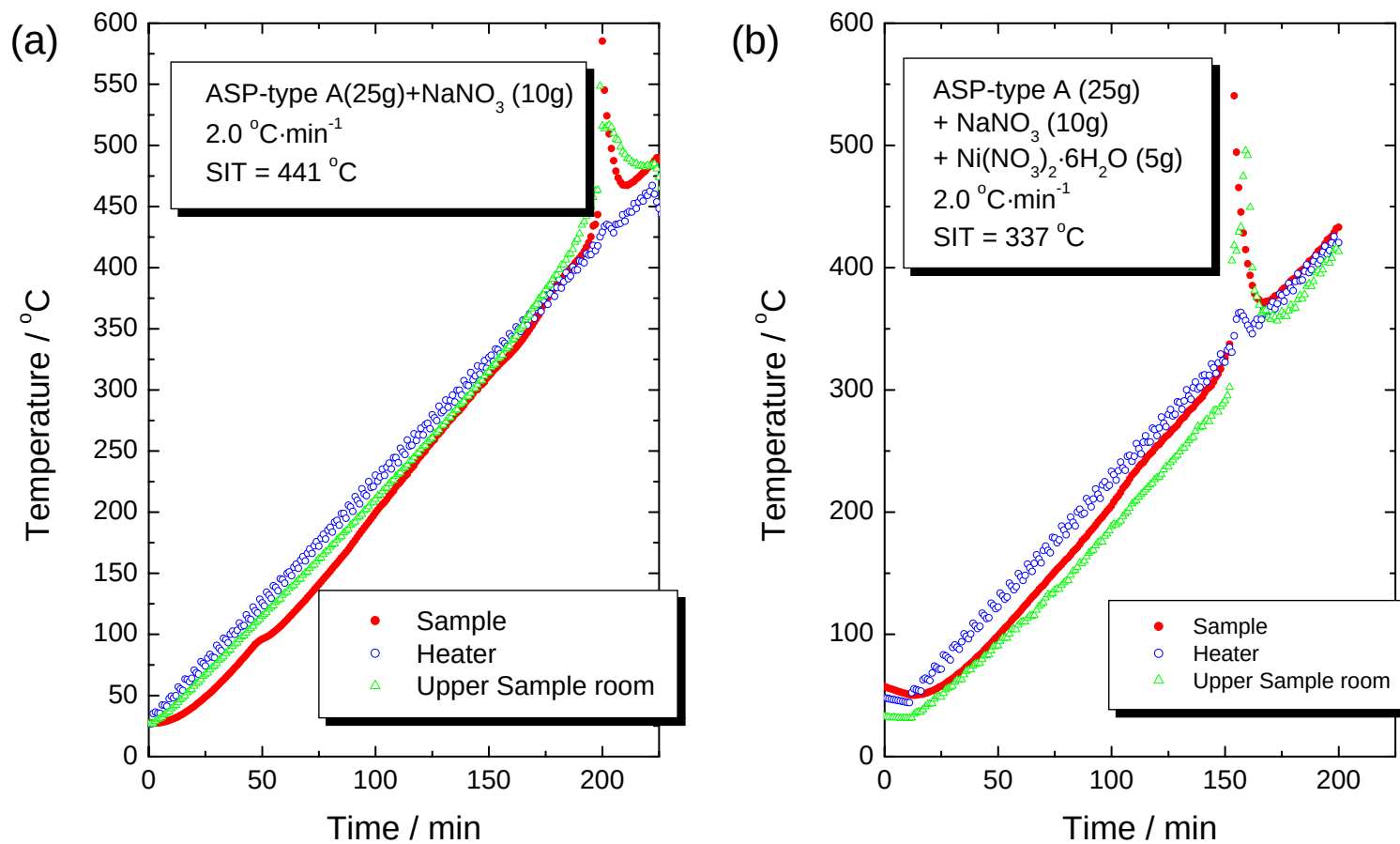


Figure 4. 4 Heating of bitumen sample with NaNO₃ (a) and Ni(NO₃)₂·6H₂O (b) at the constant heating rate

4. The self-Ignition Temperature of bitumen / nitrate mixture

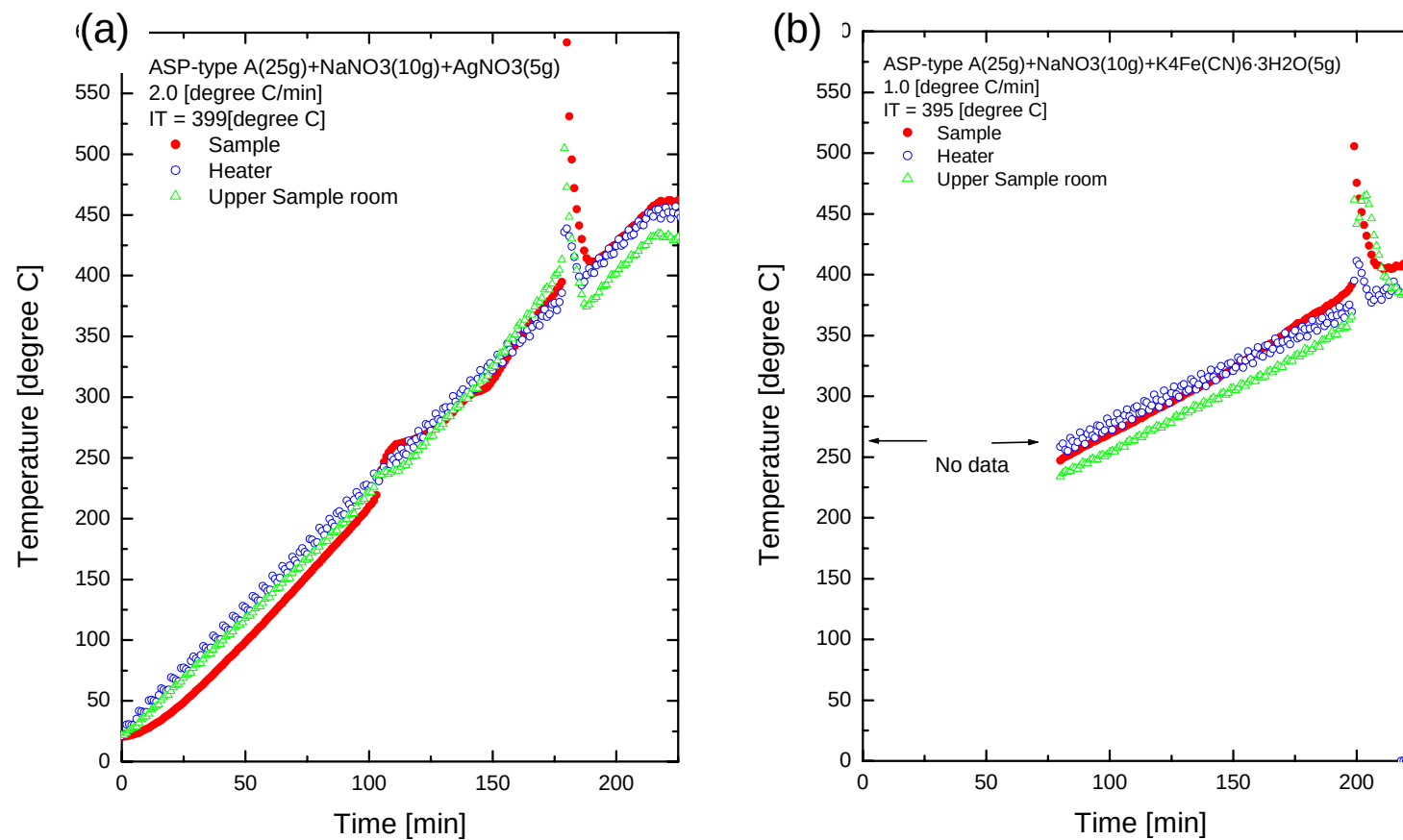


Figure 4. 5 Heating of bitumen sample with AgNO₃ (a) and K₄Fe(CN)₆·3H₂O (b) at the constant heating rate.

4. The self-Ignition Temperature of bitumen / nitrate mixture

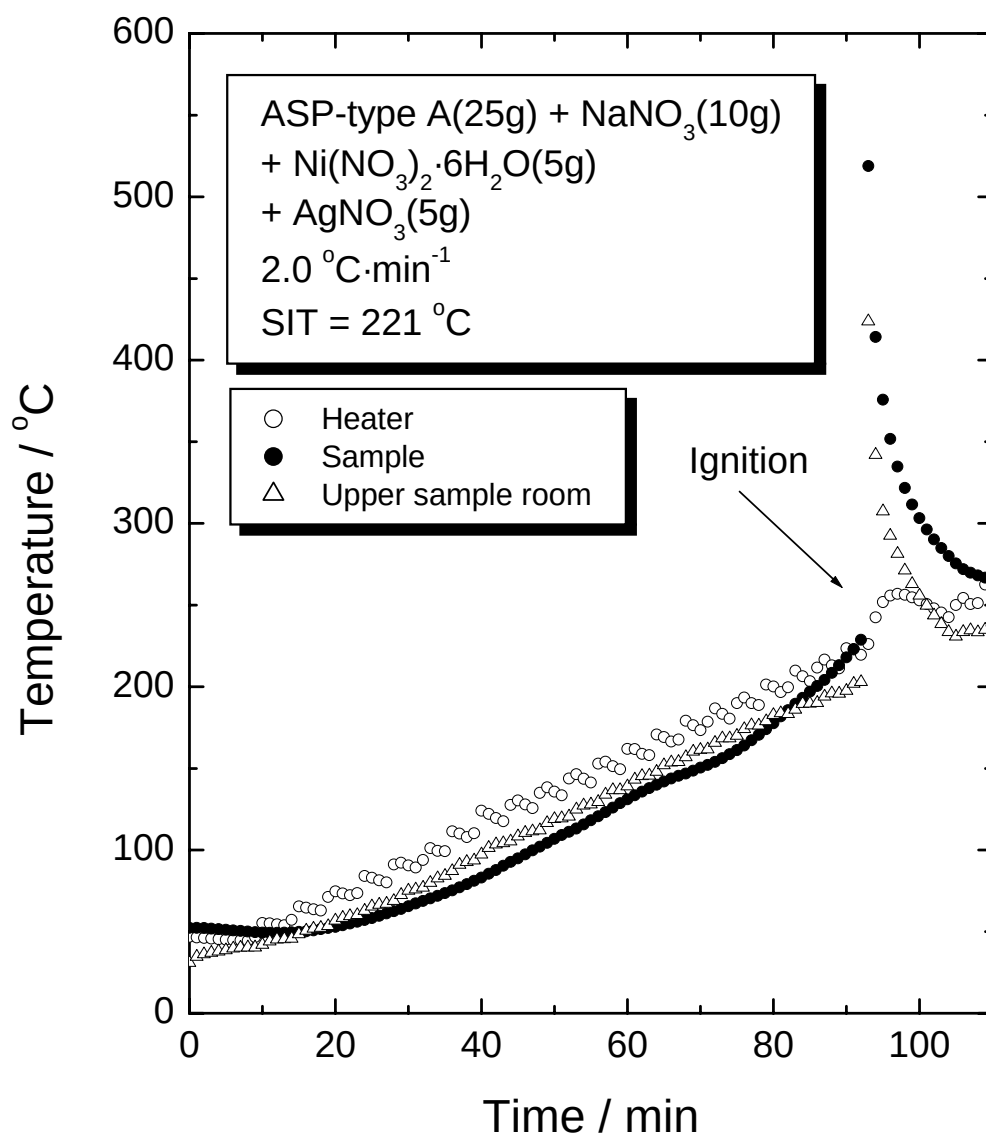


Figure 4. 6 Heating of bitumen sample with Ni(NO₃)₂ + AgNO₃ at the constant heating rate

4. The self-Ignition Temperature of bitumen / nitrate mixture

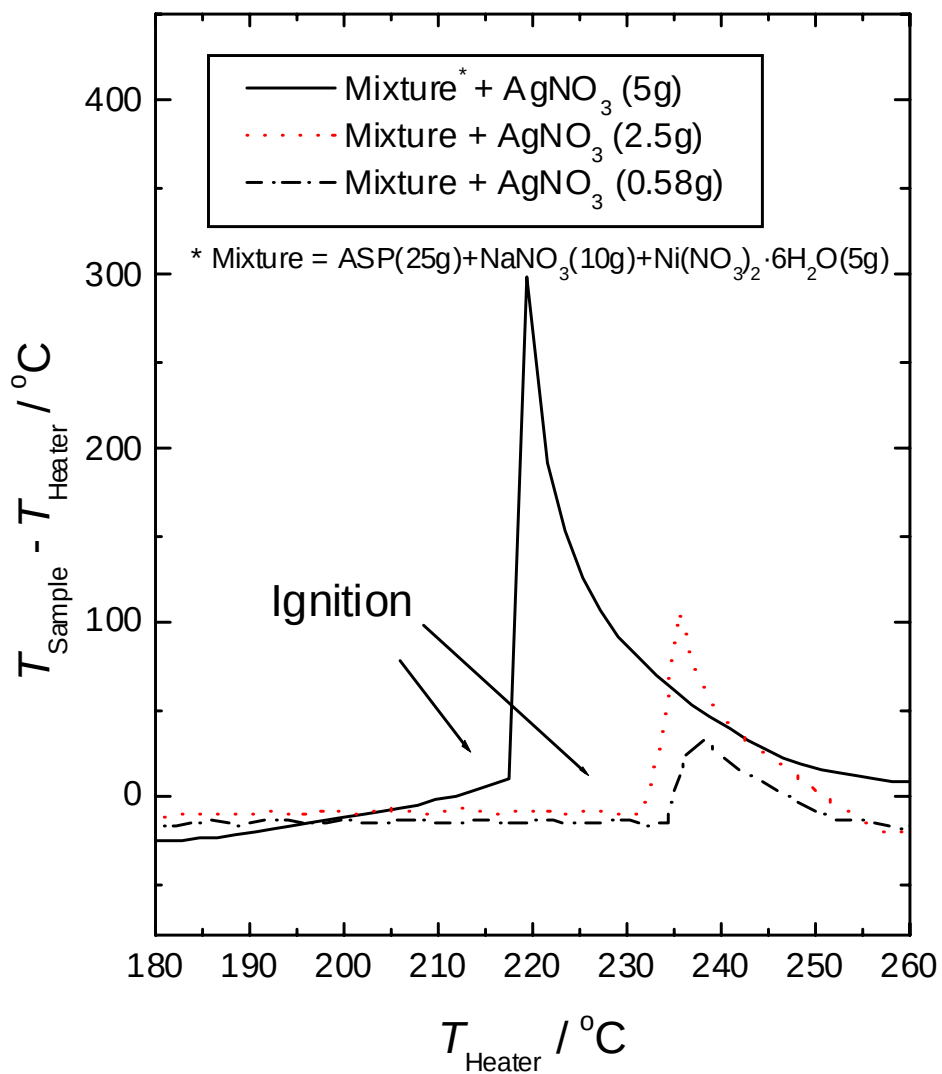


Figure 4. 7 Ignition curves of bitumen sample containing various amount of AgNO_3

4. The self-Ignition Temperature of bitumen / nitrate mixture

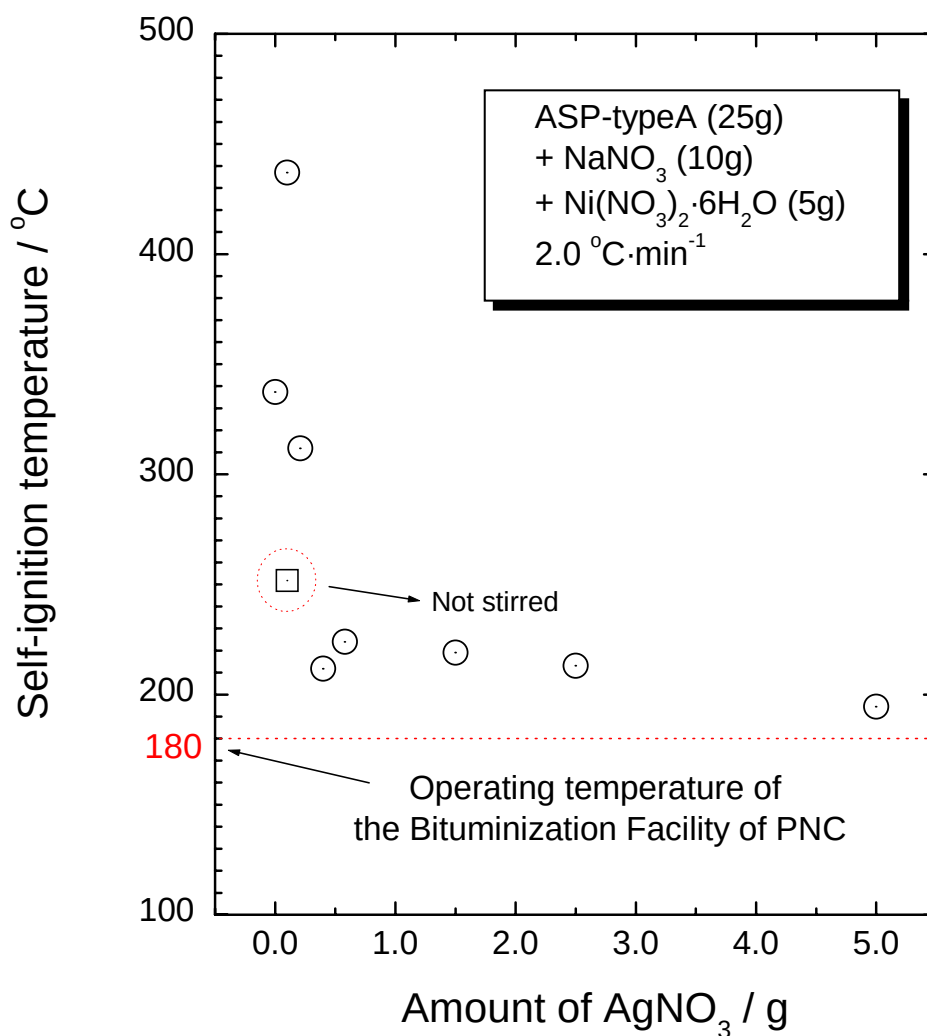


Figure 4. 8 Effects of AgNO₃ on the ignition temperature of bitumen containing NaNO₃ and Ni(NO₃)₂.

4. The self-Ignition Temperature of bitumen / nitrate mixture

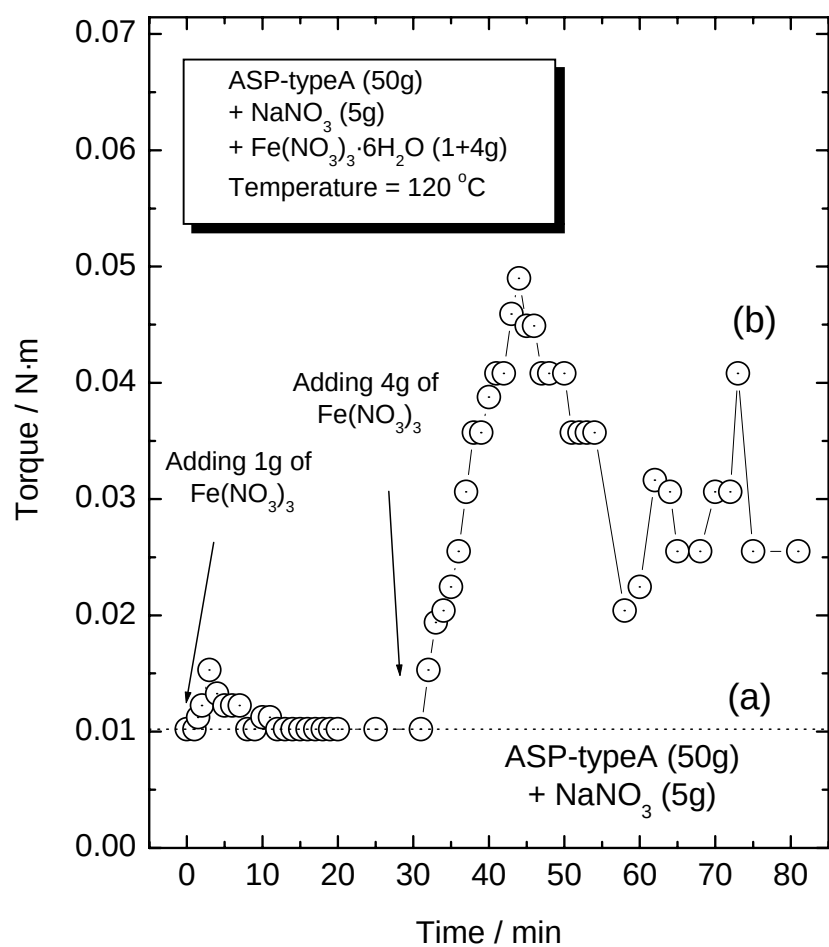


Figure 4. 9 Torque alternation of bitumen sample: ASP + NaNO₃ (a) and ASP + NaNO₃ + Fe(NO₃)₃ (b).

References

- [1] "Reports on the accident of firing and explosion at the bituminization facility in Tokai Reprocessing facility of PNC," Accident investigation Committee for the firing and explosive at bituminization facility in Tokai Reprocessing facility (Chaired by A Kanagawa) (Dec. 15,1997).
- [2] "Dictionary of chemistry 5th edition", edited by S.Nagakura *et al.*, (published by Iwanami Tokyo) in Japanese (1998).
- [3] B. Mishra, A.G. Rarez, D.L. Olson and W.A. Averil, "Formation of explosive compounds in acid-contaminated leaded rubber gloves Part I: theoretical analysis," *J. Hazard. Mater.* 56, 107 (1997).
- [4] Herrington, P R, "Oxidation of Bitumen in the presence of constant concentration of oxygen," *Petroleum Sci. and Technol.* 16(7-8), 743 (1998).
- [5] M.V. Cabanas, M. Vallet-Regi, M.Labeau and J.M. Gonzalez-Calbet, "Spherical iron oxide particles synthesized by an aerosol technique," *J. Mater. Res.* 8(10), 2694 (1993).
- [6] J. Zeger, K. Knotik, H. Jakusch: "Sedimentation technique of waste bituminization and thermogravimetric characteristics of the final products," *Management of Radioactive Wastes from Nuclear Fuel Cycle*, Vol. II, pp.113-122, IAEA-SM-207/55 (1976).

5. The formation of explosive compounds in bitumen / nitrate mixtures

5.1. Introduction

After the above-mentioned accidents, the bituminization would not be used again as a low-level radioactive treatment for reprocessing; however, these accidents have shed light on the fire hazard involved when organic waste is mixed with nitrate salts. Generally speaking, treatment of organic waste should be handled carefully in PUREX reprocessing plants.

A similar chemical accident has been reported at the USDOE's Rocky Flats Environmental Technology Site (RFETS) : an explosion occurred when leaded rubber gloves came into contact with nitric acid [4,5]. The analysis report indicated that the formation of explosive compounds must have played a role in this accident, which is another indication of the hazards involved when having organic materials, nitric acid and transition metal in close proximity.

In nuclear reprocessing plants, spent nuclear fuels are dissolved in nitric acid solutions. Some transition elements, such as Ni or Fe, may be dissolved from the vessel materials into the process streams, and nitrates of other transition metals, such as AgNO_3 , may exist in the process, because chemical reagents such as NaOH , NaNO_3 , $\text{K}_4[\text{Fe}(\text{CN})_6]$, NiSO_4 , AgNO_3 and $\text{Ba}(\text{OH})_2$, etc. are added to the waste solutions in order to immobilize long-life radioactive isotopes such as Cs, Sr and I during bituminization. If these mixtures of metal nitrates come into contact with organic materials, a fire may occur due to reactions similar to that described above, which caused the accident at RFETS.

We reported [6,7] that the combination of $\text{Ni}(\text{NO}_3)_2$ and AgNO_3 greatly reduces the self-ignition temperatures of bitumen / nitrate mixtures. In the present work, thermal analysis is performed for bitumen / nitrate mixtures that include $\text{Ni}(\text{NO}_3)_2$, AgNO_3 or AgI . In the

5. The formation of explosive compounds in bitumen / nitrate mixtures

bituminization process, radioactive iodine is converted to AgI as an insoluble treatment. Most of the Ag ions added are expected to form AgI after waste treatment in reprocessing. In order to compare the effects of adding AgNO₃ or AgI to bitumen / nitrate mixtures, the self-ignition temperatures (SIT) of bitumen / nitrate mixtures were investigated using AgNO₃ and AgI.

5.2. Experimental

5.2.1. Specification of bitumen nitrates used

PNC-type AD compound asphalt (abbreviated as ASP) was used to examine the SIT of bitumen / nitrate mixtures. Some characteristic properties [8] are given in Table 5.1. The specifications of this bitumen are expressed according to JIS (Japan Industrial Standard) regulations. Two types of samples were prepared for the present experiment: ASP + NaNO₃ + Ni(NO₃)₂ + AgNO₃ and ASP + NaNO₃ + Ni(NO₃)₂ + AgI. These chemical agents were mixed vigorously at 120°C. The sample was allowed to cool to room temperature and was then placed in the electric furnace.

5.2.2. Electric furnace for temperature measurement system

The electric furnace is illustrated in Fig. 5.1. Its temperature was controlled by a PID (proportional integral derivative) controlling power source, ULVAC Thermal Program Controller HPC-5000. The furnace containing the sample was a steel cylinder of 70 mm internal diameter and 130 mm internal height. The sample was heated at a constant rate by the heater surrounding the cylindrical sample room in which the sample beaker was placed. The heating rates varied within the range from 0.5°C/min to 4.0°C/min. The sample room was covered with KAOWOOL which is a short alumina-silica fiber product used as a thermal insulator. Temperatures in the heating apparatus were measured using five CA thermocouples covered with 316SS tubes (1.6x300 mm) as indicated in Fig. 5.1. Two of the thermocouples were attached to the outside surface of the sample room in order to measure the heater temperature. One of the thermocouples was placed just above the sample in order to monitor the temperature of the fire. The remaining two thermocouples were inserted at different places in the sample in order to make it possible to take into account the inhomogeneous temperature

5. The formation of explosive compounds in bitumen / nitrate mixtures

distribution in the sample. The thermocouples were connected to a digital voltmeter, (Kethley multimeter 2000) in order to allow the temperatures to be read. All the temperature data were fed into a personal computer through an interface. The temperature was also monitored using analog recorders that were connected directly to the thermocouples. When the sample fired, the furnace source was switched off. The SIT was read as the initiating point of the rapid heating rate period. Two thermocouples were inserted in the sample. The lower temperature of them was determined as SIT. Self-ignition was also determined to have occurred when smoke was detected. The initial masses of bitumen, NaNO_3 , $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and AgNO_3 of the reagent were fixed as 25 g, 10 g, 5 g and 1 g, respectively.

5.3. Results and Discussion

5.3.1. Ignition temperature of bitumen / nitrate mixture

Table 5.2 shows the SIT for the five samples. For the AgI additive, the SITs are independent of the 0.5 and 2.0°C/min heating rates. In contrast to the AgI additive, the SIT of AgNO_3 additives decreased significantly when the heating rate was changed from 4.0 to 0.5°C/min.

Figure 5.2 shows the temperature change curves of the ASP + NaNO_3 + $\text{Ni}(\text{NO}_3)_2$ + AgNO_3 sample under three different heating rates. The ignition of the sample can be detected by the jump in temperature. As the heating rate increases, the ignition temperature increases. At the heating rate of 4.0°C/min, ignition occurs at 300°C, followed by a very rapid temperature increase of 300 °C, up to 600 °C.

Figure 5.3 shows the relationship between the ignition temperature and the heating rate. At a heating rates below 2.0°C/min, the SIT is approximately 210°C, whereas at heating rates higher than 2.0°C/min, the SIT is approximately 300°C.

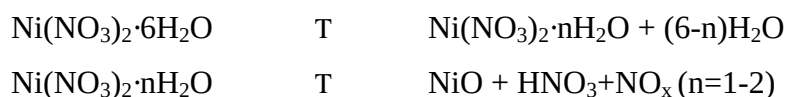
5.3.2. Formation of explosive compounds in bitumen / nitrate mixture

Clerc and O'neal[9] reported that asphalt consists of three types of agents, namely asphaltenes, resins and oils. The molecular weight (ebullioscopic) of the asphalt they

5. The formation of explosive compounds in bitumen / nitrate mixtures

examined, which consists of C-84.1, H-8.9, S-4.6, N-0.7 and O-1.8 (mole %), is 1260. The m/e value measured by mass spectrometry ranges from 24 to 1900. Thus, this asphalt is assumed to contain a lot of $>C=C<$ double bonds and aromatic compounds. Although the specifications of the asphalt used in the present work are different from those of the asphalt examined by Clerc *et al.*, both types of asphalt are considered to have similar chemical compositions.

In the following discussion on the chemical reactions involved in the present firing process, ignition is assumed to occur through two primary steps, i.e. the generation of HNO_3 or NO_x gases from $Ni(NO_3)_2$ and the formation of explosive or initiator materials. Concerning the former process, since $Ni(NO_3)_2 \cdot 6H_2O$ is very hygroscopic, crystal water is released in the range from 100 to 200°C and hydrated $Ni(NO_3)_2$ is decomposed to $NiO + HNO_3 + NO_x$ at temperatures above 200 °C as[6,7]



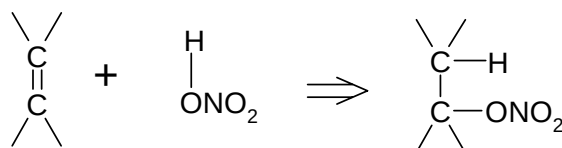
With respect to the latter step or the formation of explosives, Urbanski[10] reported that eight definite structural groupings exist in general explosive materials, as listed below.

- (b) (1) $-NO_2$ and $-ONO_2$ in both organic and inorganic materials;
- (c) (2) $-N=N-$ and $-N=N=N-$ in organic and inorganic azides;
- (d) (3) $-NX_2$, where X is a halogen, as in NCl_3 ;
- (e) (4) $-C \equiv N-O$ in fulminates;
- (f) (5) $-OClO_2$ and $-OClO_3$ in organic and inorganic chlorates and perchlorates;
- (g) (6) $-O-O-$ and $-O-O-O-$ in organic and in organic peroxides and ozonides, respectively;
- (h) (7) $-C \equiv C-$ in acetylene and metal acetylides;
- (i) (8) $M-C$, metal bonded with carbon in some organometallic compounds.

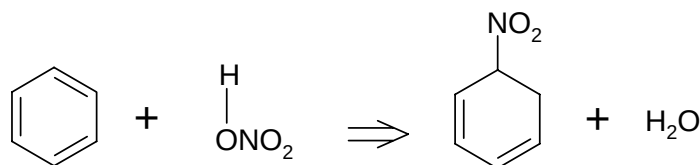
The original bitumen asphalt and nitrate salts do not contain $-N=N-$ bonds nor halogens. Since peroxide compounds are not formed in the presence of HNO_3 , the chemical species of (6) may be excluded. Thus the reactive groups (2), (3), (5), (6), (7) and (8) can be eliminated as possible initiating chemicals. The remaining, reactive groups, (1) and (4), may be generated in the oxidation process in hydrocarbon- HNO_3 mixtures.

5. The formation of explosive compounds in bitumen / nitrate mixtures

In the case of the compound (1), asphalt has many double bonds ($>C=C<$) that react with inorganic acids such as HNO_3 and form $C=O$ groups. The nitric acid produced from $Ni(NO_3)_2 \cdot 6H_2O$ is assumed to react with the olefin hydrocarbons and benzene. Michael and Carlson[11] reported the following nitration process, in which nitric acid, as $H + ONO_2$, is considered to react with double bonds.

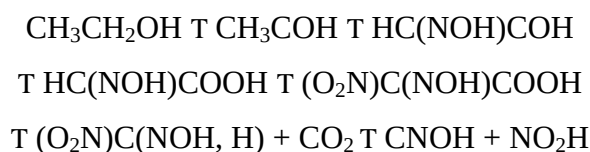


Generally the nitration process proceeds easily in the presence of aromatic compounds. The reaction process is as follows:



These compounds are generally expected to be generated in bitumen. However, as mentioned in the introduction, the combination of $Ni(NO_3)_2$ and $AgNO_3$ has been found to greatly reduce SITs, and the above-mentioned nitro compounds would not explain the effect of silver nitrate.

In the case of compound (4), $AgCNO$ is expected to form. The mechanism of formation of fulminate ions from alcohol and nitric acid has been discussed by Wieland[12], who described the formation process as follows.



Wentrup [13] reported that fulminate can form from cyclic compounds. A new synthesis of fulminic acid from 4-substituted isoxazol-5(4*H*)-ones was confirmed. Although the reaction described in the present study has not yet been clarified, this reaction appears to be similar to that described by Wentrup.

Singh[14] has studied ultra violet spectra of fulminates and has suggested, based on quantum calculations, that the most probable structure of fulminates may be $-O-N \equiv C$. However, his conclusions were not entirely correct. Briton and Duniz[15] reported that crystal

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structures of AgCNO occur in two polymorphic forms: one is orthorhombic and trigonal with a rhombohedral lattice.

P.H. Collins *et al.* [16] reported that the temperature of ignition for silver fulminate is in the range between 200 and 204°C. These results are very similar to the lowest result of the present work. Generally, fulminate forms compounds with the following cations[17] : Na⁺, K⁺, NH₄⁺, Rb⁺, Mg²⁺, Ca²⁺, Sr²⁺, Ba²⁺, Cu²⁺, Ag⁺, Au⁺, Tl⁺, Zn²⁺, Cd²⁺ and Pb²⁺. If a certain amount of these cation reagents is present, the bitumen nitrate mixture can ignite at low temperatures.

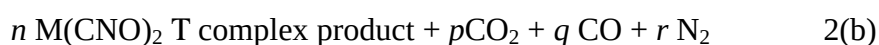
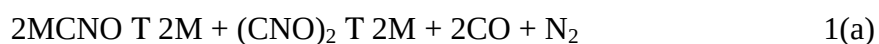
In the present work AgI additive bitumen nitrate mixture has shown the higher SIT of 300°C while AgNO₃ additive mixtures have shown low SIT depending on the heating rate. If we assume that fulminate is initiator of the firing, formation reaction of silver fulminate is expressed by



AgNO₃ is a very soluble salt in aqueous solution. This means AgNO₃ is fully dissociated in the forms of NO₃⁻ and Ag⁺ ions hydrated with water molecules. When NO_x gas is generated in the system, Ag⁺ easily makes complex with NO_x. On the other hand AgI is known with its small solubility and is considered to exist in the forms of solid on critical state. Therefore it is conceived that AgI does not form easily complex with NO_x species released at around 200°C. At higher temperatures of about 300°C, probably dissociation of AgI is enhanced and disassociated Ag⁺ or Ag is conceived to become the initiation materials of the firing.

5.3.3. Decomposition model of explosives

It is probable that the following chemical process occur in the decomposition of the monovalent and divalent metal fulminates studied so far:



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When self-propagation decomposition occurs, reaction probably takes place according to process 1(a, b) in all fulminates. On the other hand, in the slow decomposition, processes 1(a, b) and 2(a, b) are probably involved to varying degrees.

To establish what stage is the rate-determining step, is essential for describing the kinetics of the decomposition of complex chemical systems that occur through several stages. Therefore, in practice, the behavior of such systems are described according to their heating, which is known as the formal kinetic approach. Such an approach does not consider each stage of the process separately, but rather the average process is considered without describing the mechanisms of the interim stages. Thus, a formal kinetic equation is used to describe the rate of this average process.

If the amount of the explosive compound is assumed to be the same at different temperatures, the following equations are generally used [18,19]. These equations were basically introduced by Ozawa[20]. The decomposition of explosives is a first-order reaction.

$$-\frac{dx}{dt} = kx \quad (1)$$

where t is the time, x is the fractional weight of the reacting materials, and k is the kinetic constant. The relationship between the kinetic constant (k) and the absolute temperature (T) of the reaction is expressed using an Arrhenius equation

$$k = A \exp\left(-\frac{E_a}{RT}\right) \quad (2)$$

where A is the pre-exponential constant, E_a is the activation energy, and R is the gas constant (J/mol K). The temperature change is represented by

$$T = T_0 + at \quad (3)$$

where T is the absolute temperature, T_0 is the starting temperature (K), and a is the heating rate in K/min.

Even when the amount of x is unknown, the activation energy of the thermal behavior of the property can be estimated using the following equations:

$$-\int_{x_0}^x \frac{dx}{x} = \frac{A}{a} \int_{T_0}^T \exp\left(-\frac{E_a}{RT}\right) dT \cong \frac{A}{a} \int_0^T \exp\left(-\frac{E_a}{RT}\right) dT \quad (4)$$

where T_0 and x_0 are T and x at $t=t_0$, respectively. Ordinarily, the rate of reaction is very low at low temperatures. Therefore, this approximation is valid. The values of the right-hand side of

5. The formation of explosive compounds in bitumen / nitrate mixtures

equation (4) have been calculated and tabulated by Doyle [21]. If E_a/RT is larger than 20, the following approximation is applicable [22].

$$\log\left(\frac{R}{E_a} \int_0^T \exp\left(-\frac{E_a}{RT}\right) dT\right) \cong -2.315 - 0.4567 \frac{E_a}{RT} \quad (5)$$

The left-hand side of equation (4) is a constant which does not depend on the heating rate. From equations (4) and (5), the following equation is obtained:

$$\log a = -0.4567 \times \frac{E_a}{RT} + \text{Const.} \quad (6)$$

Plotting $\log a$ with respect to $1/T$ yields a slope of $E_a \times 0.4567/R$. The experimental results of Fig. 5.3 are replotted in Fig. 5.4, in which $\log a$ is plotted with respect to $1/T$. The experimental data show the linear relationship expressed by the Arrhenius equation in Fig. 5.4. Thus, the activation energy E_a is obtained from the slope as 30 kJ/mol using a least squares fitting of the plots in Fig. 5.4.

These results show that the decomposition of explosive compounds, or ignition, can be explained by general kinetic thermal analysis. Singh [23] reported the activation energy of 27.0 kJ/mol for the first-order reaction of the explosive compounds of silver fulminate. The activation energy obtained in the present work is well in accordance with the value obtained by Singh and supports the previous discussion where silver fulminate is presumed as the initiator of the self-ignition.

5.4. Conclusion

Self-ignition temperatures (SITs) of PNC type bitumen- NaNO_3 mixtures were measured in the presence of $\text{Ni}(\text{NO}_3)_2$ and Ag compounds (AgNO_3 or AgI). The SIT of bitumen mixtures involving AgNO_3 is dependent on the heating rate: The smaller the heating rate, the lower the temperature at which bitumen nitrate mixture ignites. In contrast, the SIT of bitumen mixtures containing AgI does not depend on the heating rate. The activation energy E_a for the ignition of bitumen / nitrate mixtures has been calculated to be 30 kJ/mol. This value is in close agreement with the currently accepted decomposition activation energy for the first-order reaction of silver fulminates. Furthermore, the SIT of bitumen mixture has been found to be similar to the ignition temperature of silver fulminate reported by Collins *et al.*

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[16] Therefore, silver fulminate is presumed to be the initiator of the self-ignition of the bitumen nitrate mixture involving AgNO_3 .

5. The formation of explosive compounds in bitumen / nitrate mixtures

Table 5. 1 Specifications of the asphalt used in the present study

Testing	Methods	Results
Softening point [°C]	JIS K 2207	82
Penetration distance* at 25°C, 100 g, 5 s [mm]	JIS K 2207	3.6
Penetration Index	-	3.8
Evaporation mass variation percentage [%]	JIS K 2207	0.02
Flash point, Cleveland Open Cup [°C]	JIS K 2265	316
Solubility in trichloroethane [%]	JIS K 2207	99.47
Ductility at 25°C [cm]	JIS K 2207	4
Density at 25°C [g cm ⁻³]	JIS K 2249	1.018

* "Penetration" is defined as the penetration distance expressed by the unit of 0.1 mm.

Thus the penetration of the present asphalt is 36.

5. The formation of explosive compounds in bitumen / nitrate mixtures

Table 5. 2 Ignition temperature difference of AgNO₃ and AgI at different heating rate.

Additive salts ^{*1}	Heating rate [°C·min ⁻¹]	SIT ^{*2} [°C]
AgNO ₃ (1.0g)	4.0	307
AgNO ₃ (1.0g)	1.8	221
AgNO ₃ (1.0g)	0.5	208
AgI (5.0g)	2.0	319
AgI (5.0g)	0.5	312

***1 Sample = PNC-ASP(25g) + NaNO₃ (10g) + Ni(NO₃)₂ (5g) + additive salt**

***2 SIT= Self-ignition temperature**

5. The formation of explosive compounds in bitumen / nitrate mixtures

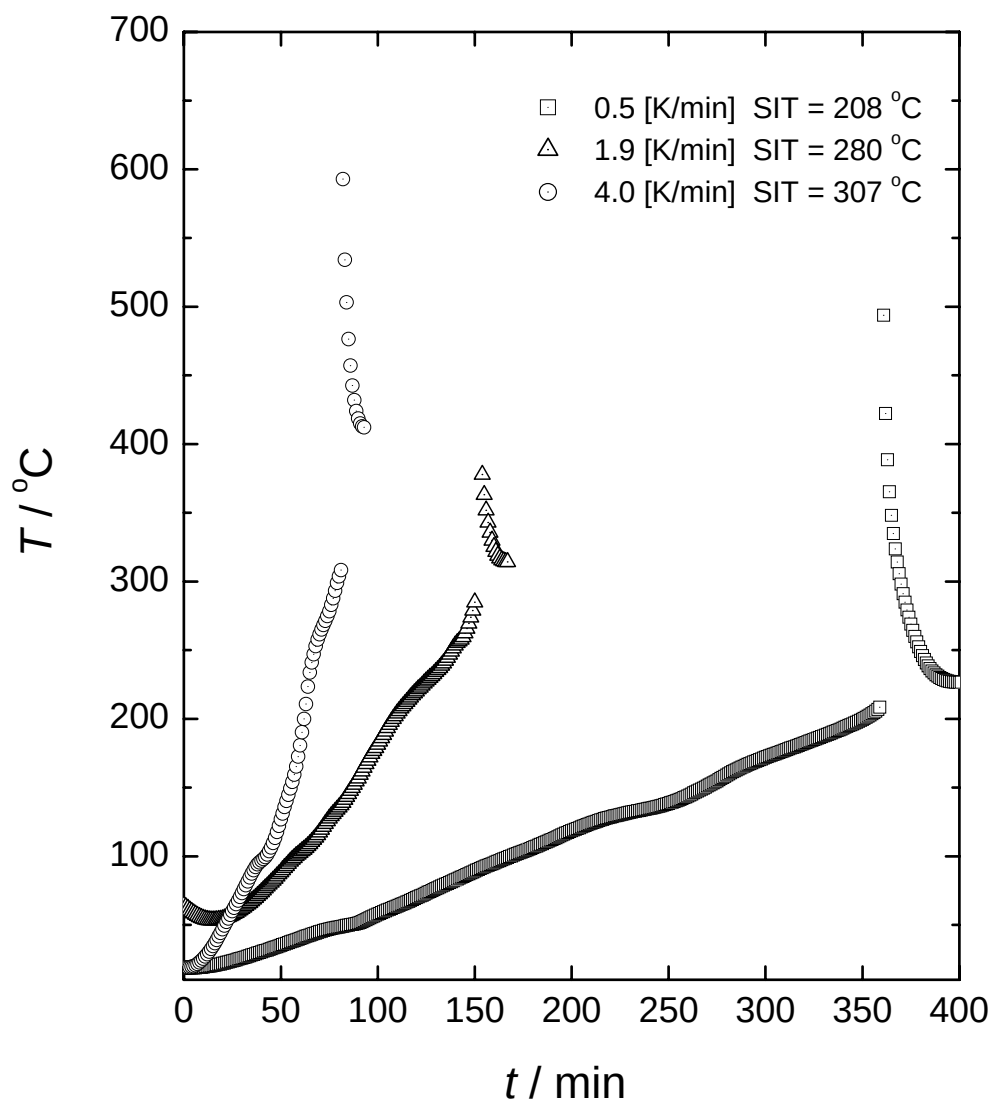


Figure 5. 1 Self-ignition curves for different heating rates for a bitumen sample (ASP(25g)+NaNO₃(10g)+Ni(NO₃)₂(5g)+AgNO₃(1g))

5. The formation of explosive compounds in bitumen / nitrate mixtures

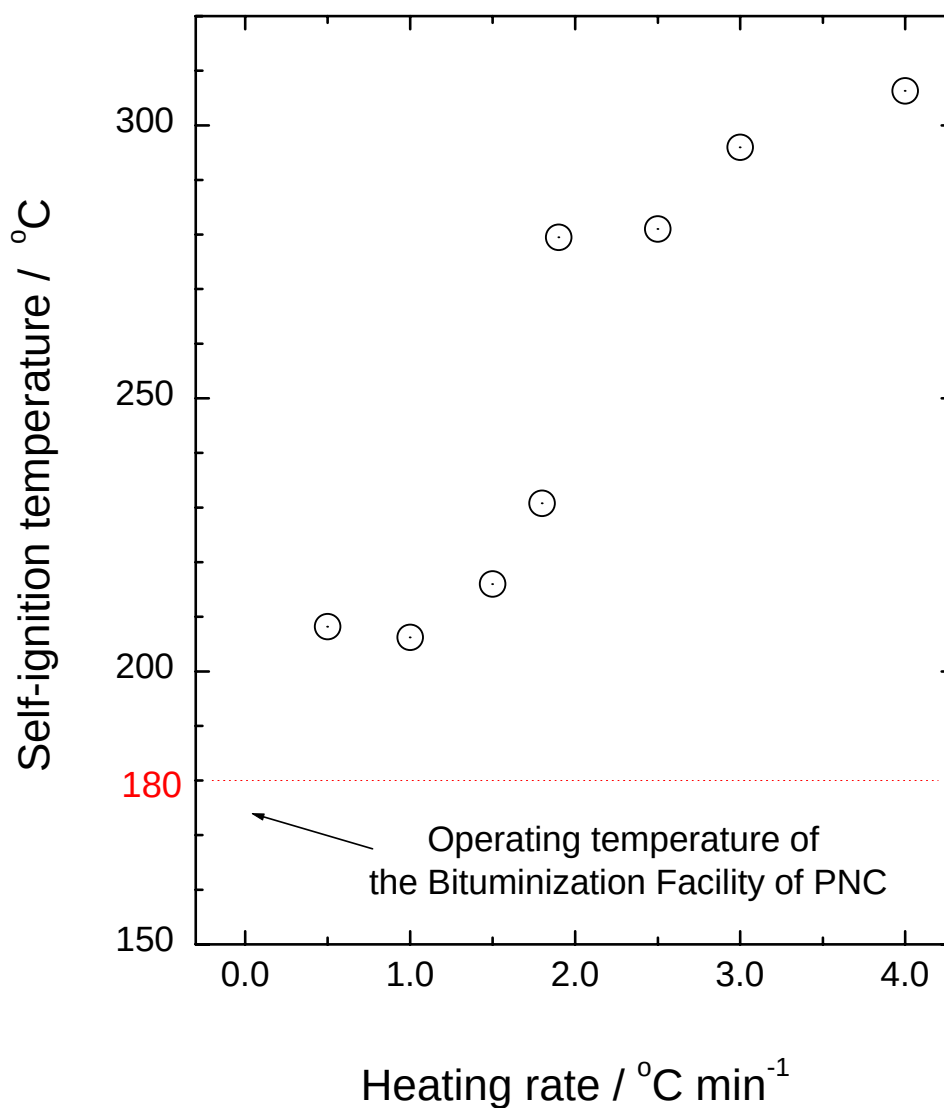


Figure 5. 2 Relationship between self-ignition temperature and heating rate for a bitumen sample (ASP(25g) + NaNO₃(10g) + Ni(NO₃)₂(5g) + AgNO₃(1g))

5. The formation of explosive compounds in bitumen / nitrate mixtures

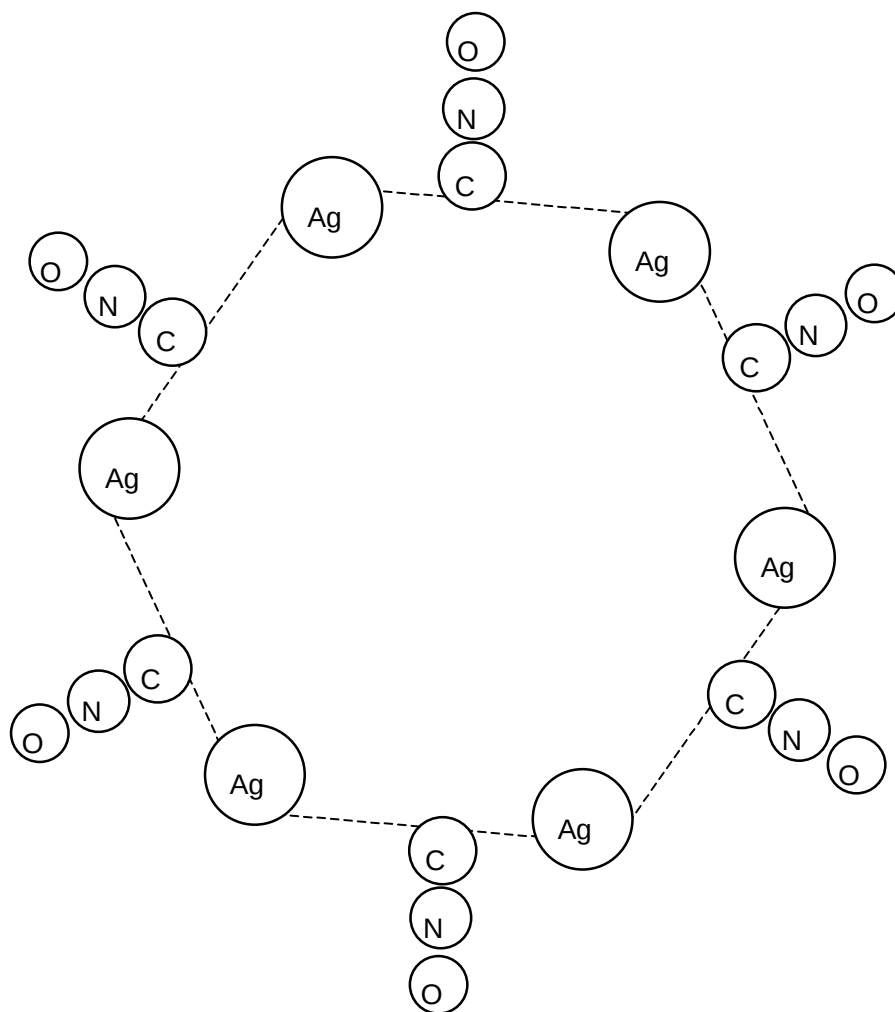


Figure 5. 3 Rhombohedral silver fulminate. View: down hexagonal *c* axis.

5. The formation of explosive compounds in bitumen / nitrate mixtures

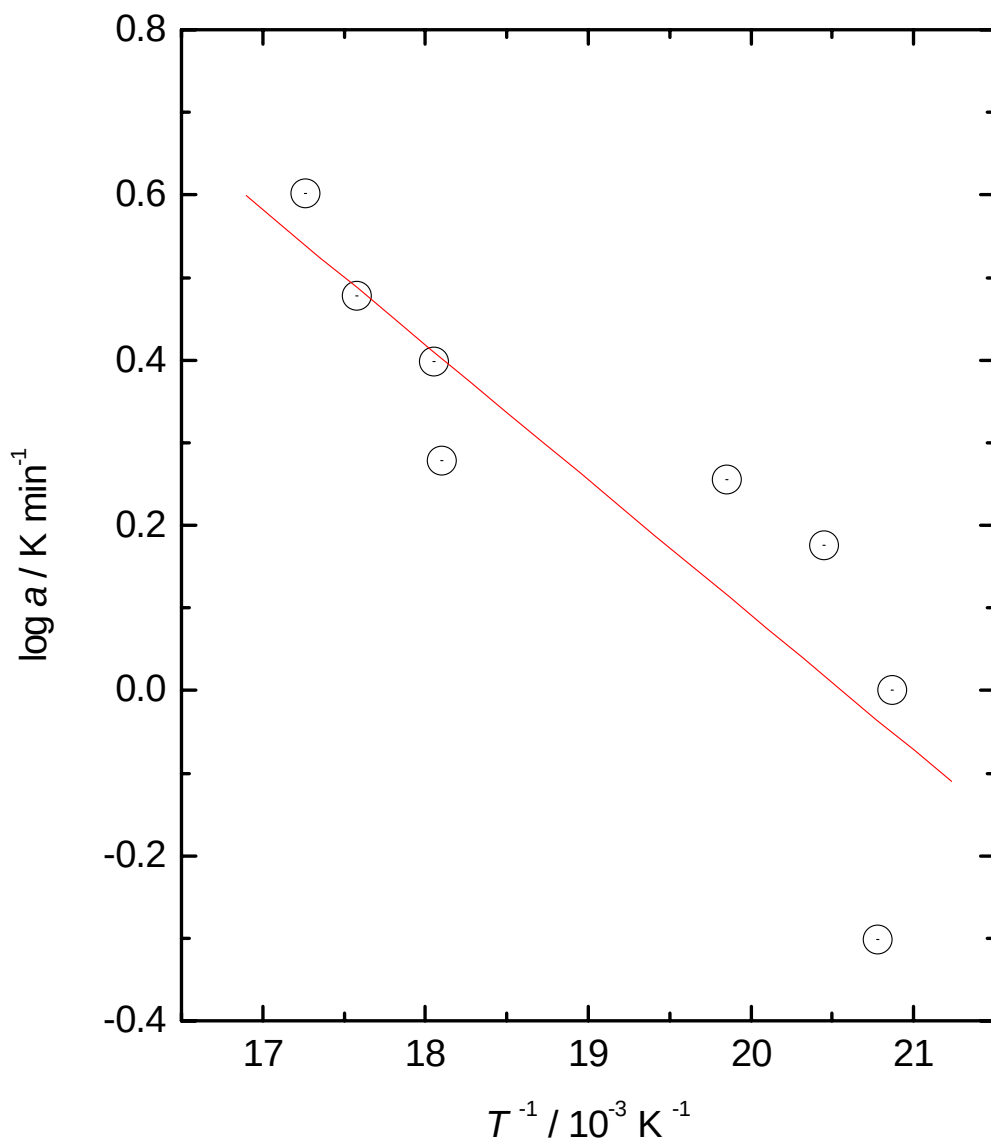


Figure 5. 4 Relationship between the logarithm heating rate and the inverse of self-ignition temperature

5. The formation of explosive compounds in bitumen / nitrate mixtures

References

- [1] M. Demonie, E. Detilleux, H. Eschrich, W. Hild, A. Osipenco and R. Reynders, The fire incident in the eurobitum plant on december 15, 1981 : Description, Evaluation and Conclusions, ETR-314, Eurochemic, Belgium, December 1990.
- [2] N. Sasaki, T. Koyama, E. Omori, A. Maki and T. Yamanouchi, Study on the cause of the fire and explosion incident at Bituminization Demonstration Facility of PNC Tokai Works, SPECTRUM'98, Vol.III, Denver, CO, 1998, pp. 67-77.
- [3] Incident Investigation Committee, The fire and explosion incident at the Bituminization Demonstration Facility of PNC Tokai Works (in Japanese), 1997.
- [4] B. Mishra, A.G. Rarez, D.L. Olson and W.A. Averil, Formation of explosive compounds in acid-contaminated leaded rubber gloves Part I: theoretical analysis, J. Hazard. Mater., 56 (1997) 107-116.
- [5] B. Mishra, A.G. Rarez, D.L. Olson and W.A. Averil, Formation of explosive compounds in acid-contaminated leaded rubber gloves Part II: Experimental verification, J. Hazard. Mater., 57 (1998) 13-28.
- [6] K. Okada, M. Nomura and Y. Fujii, Ignition temperature of bitumen nitrate mixture : Additive Salts Segregation Effects, SPECTRUM'98, Vol.II, Denver, CO, 1998, pp. 1129-1134.
- [7] K. Okada, M. Nomura and Y. Fujii, The self-ignition temperatures of bitumen mixtures containing transition metal nitrates, Nuclear Technol., (1999) in press.
- [8] Showa Shell Corporation, Specification of AD compound asphalt, Lot.No.90514, 1997.
- [9] R.J. Clerc and M.J. O'neal, Jr., The mass spectrometric analysis of asphalt, Anal. Chem., 33 (1961) 380-382.
- [10] T. Urbanski, Chemistry and Technology of Explosives, Vol.I, PWN-Polish Scientific Publishers, Warsaw, 1964.
- [11] A. Michael, and G.H. Carlson, On the mechanism of the nitration process, J. Am. Chem. Soc., 57 (1935) 1268-1276.
- [12] H. Wieland, Eine neue Knallsäuresynthese. Über den Verlauf der Knallsäurebildung aus Alkohol und Salpetersäure, Chem. Ber., 40 (1907) 418-422.
- [13] C. Wentrup, B. Gercht and H. Briehl, A new synthesis of fulmic acid, Angew. Chem. Int. Ed. Engl., 18 (1979) 467-468.
- [14] K. Singh, Structure of fulminate ion, J. Chem. Soc., (1959) 459-461.

5. The formation of explosive compounds in bitumen / nitrate mixtures

- [15] D. Britton and J.D. Dunitz, The crystal structure of silver fulminate, *Acta Cryst.*, 19 (1965) 662-668.
- [16] P.H. Collins and K.J. Holloway, A reappraisal of silver fulminate as a detonant, *Propellants and Explosives*, 3 (1978) 159-162.
- [17] S. Nagakura *et al.* (Eds.), *Encyclopedia of Chemistry and Physics*, 5th edn, Iwanami, Tokyo, 1998.
- [18] H.E. Kissinger, Reaction kinetics in differential thermal analysis, *Anal. Chem.*, 29 (1957) 1702-1706.
- [19] J. Li, X. Wang, R. Hu, B. Kang, Y. Ou and B. Chen, The thermal behavior of powder emulsion explosives, *J. Thermal Anal.*, 45 (1995) 261-268.
- [20] T. Ozawa, A new method of analyzing thermogravimetric data, *Bull. Chem. Soc. Jpn.*, 38 (1965) 1881-1886.
- [21] C.D. Doyle, Kinetic analysis of thermogravimetric data, *J. Appl. Polymer Sci.*, 5 (1961) 285-292.
- [22] C.D. Doyle, Estimating isothermal life from thermogravimetric data, *J. Appl. Polymer Sci.*, 24 (1962) 639-642.
- [23] K. Singh and G.D. Palkar, Solid-phase reactions in silver fulminates, *J. Chem. Soc.*, (1965) 1474.

6. The flame-propagation of the bitumen / nitrate mixture

6.1. Introduction

The bituminization has been implemented in the Tokai reprocessing plant to solidify low-level liquid waste (LLW). The wastes mainly contain nitrate salts released from the PUREX process where the spent fuel is dissolved in the nitric acid. In the bituminization several chemical reagents are added to immobilize the radioactive isotopes of Cs, Sr and I. The most advantage of the bituminization of the LLW is as follows:

- (1) The high resist-penetration against water.
- (2) The high reduction effect of capacity.

Normally, the bituminized solid product has the waste 40-60 w/o against the bitumen. The bituminization plants have been working in the nuclear power plants in many countries and the reprocessing plant in Europe, Japan and Russia. It is known that bituminization has defects of firing. Especially the bituminization plant working in the reprocessing plant is very dangerous because the waste contains nitrates. The information is listed in Table 6.1[1,2].

In Japan, bituminization facility of the Tokai reprocessing plant has produced 30,000 drums of products since 1982. However, on March 11, 1997, bituminization demonstration facility caused a fire and an explosion incident. Although the radiological effects of the accident to the public were negligible, the accident caused a great shock to the public and gave an influence on the national nuclear development programs. While the report of accident was described by the investigation group for the incident on December 15, 1997 after holding meetings thirty times, there still remain some issues to be clarified especially for the cause of the fire from physical and chemical points of view.

6. The flame-propagation of the bitumen / nitrate mixture

There were some accidents not only in the Japanese facility but also in Belgium, France and Germany. In Japan, the treatment of the LLW using bituminization will not be done again. However, bituminization facilities are working all over the world. There will be a possibility of accident somewhere. If the ignition occurred in the part of the steel drum and did not continue to burn out the whole steel drum, the accident did not occur.

A lot of reasons for the accidents were predicted; in the present study, the model is focused on the segregation of metal nitrate salts. A part from the accident investigation committee, the present work points out that a mixture of (Ag, Ni)-nitrates + organic (bitumen) is very hazardous material which easily ignites itself even at low temperature. This is due to the formation of nitro compounds and explosive compounds. It is found that the self-ignition temperature (SIT) depends on the chemical composition and heating rate. In the present paper it has not pointed out that the direct cause of accident, but some dangerous factors in the PUREX reprocessing. Normally, a lot of NaNO_3 was contained in the bituminization process, and $\text{Ni}(\text{NO}_3)_2$ may exist in the case of corrosion of the piping materials. AgNO_3 can be accidentally present in the case of improper handling of an iodine immobilizing agent, the possibility of the segregation of large amount of Ag or Ni nitrate is very low in the normal condition of the operation. The additive chemical agents of Ag and Ni nitrates considerably decrease the SITs; we have to clarify the whole behavior relating to the bitumen nitrate mixtures. We should also clarify the chain reaction limit of bitumen / nitrate mixtures at various conditions from the viewpoint of safety engineering. Thus it has been conducted that the experimental work on the chemical reactions or the flame propagation of the bitumen nitrate mixtures.

In this chapter two types of experiments are conducted. In one experiment $\text{Ni}(\text{NO}_3)_2$ exists in the center part (Model-A), another was that $\text{Ni}(\text{NO}_3)_2$ existed at the dispersed condition (Model-B). To establish an easy analysis, AgNO_3 was segregated in the center of the sample to start firing from the center of the sample and then the fire spread in the radial direction.

Concerning these two types of samples, a question is raised, “In which condition does the flame all over the sample material?” (In which condition does a chain reaction occur?) Thus, in the present chapter, the flame propagating behavior and the speed of the flame propagation are experimentally examined. In addition, the chemical condition of bitumen /

nitrate mixture was investigated using Fourier transfer-infrared spectroscopy (FT-IR) in terms of the reaction between -NO_2 and aromatic compounds.

6.2. Experimental

6.2.1. Temperature measurement and furnace system

Temperatures were measured by more than seven-channel thermocouples. Seven-channels were used for inside measurement of the sample; the rest two-channels were used for the surface temperature of the furnace and the atmosphere of the furnace. The experimental temperature was measured with a Chromel-Alumel (CA) thermocouple (Fig.6.1). The thermocouple was covered by Type 316 stainless steel (SS316: $\phi 1 \times 500 \text{ mm}$). Its cold junction was located in a thermos bottle filled with ice. The sensor was calibrated against a standard thermocouple in ice. Temperature was recorded every 0.08 s/channel from start to ignition by the digital multimeter (DMM) and relay unit. Heating speed of the furnace was controlled by the PID regulator.

6.2.2. Sample preparation and two possible models of the burnable bituminized products at low temperatures

ASP was added with NaNO_3 and $\text{Ni(NO}_3)_2$ at room temperature and then elevated to 120°C to be mixed easily. The softened sample was stirred to mix homogeneously. The sample was cooled down.

In the normal condition, the bituminized product consists of two materials, i.e., asphalt and salts. The salts mainly consist of metal nitrates. It has found that the bituminized products ignite at low temperature when some metal nitrates are segregated. Fig. 6.1 shows the two models of the bituminized products. One is that the nitrate salts were segregated only in the center part, which was defined as “Model-A”. The other is that abnormal type of metal nitrates existed under dispersed condition, which was defined as “Model-B”. Here the abnormal salt is defined as $\text{Ni(NO}_3)_2$, because it is previously found that $\text{Ni(NO}_3)_2$ made bituminized products fire at low temperature. It is known that if AgNO_3 is segregated at the center part of the sample, ignition starts from the part where AgNO_3 was present.

6.2.3. Fourier transform infrared spectrometry (FT-IR)

Fourier transfer infrared spectroscopy (FT-IR) was used to observe the chemical reaction between ASP and metal nitrates. The samples of the following four types were prepared:

- (a) ASP
- (b) Mixed metal nitrates (NaNO_3 (0.5g) + $\text{Ni}(\text{NO}_3)_2$ (0.5g) + AgNO_3 (1g))
- (c) ASP + Mixed metal nitrates (195 °C 13h for purified by methanol)
- (d) Burned ash (ASP + Metal nitrates, 220 °C ignite itself)

The sample (a) is asphalt used in this work. The sample (b) is metal nitrate used in this work. The sample(c) was prepared as follows. ASP (1g), NaNO_3 (0.5g), $\text{Ni}(\text{NO}_3)_2$ (0.5g) and AgNO_3 (1g) were mixed with each other. The sample (c) was heated under air atmosphere at 195 °C which was kept for 13 hours. After cooling down, the sample (c) was dissolved in methanol and dried out under vacuum to remove non-oil component. The sample (d) was a mixture of burned ash of ASP (25g), NaNO_3 (10g), $\text{Ni}(\text{NO}_3)_2$ (5g) and AgNO_3 (5g). To analyze the characteristic of the sample (a), (b), (c) and (d), a Furrier-transform infrared spectrometer (FT-IR a JASCO FT/IR-410) was employed using a KBr disc ($\phi 10 \times 1 \text{mm}$) method with 0.2% of the sample. The sensitivity of wavenumber was 1.0 cm^{-1} and the scan speed was 2 mm/s. The number of integration of FT was 16 times. These four results yielded the information how asp and metal nitrates react.

6.3. Results and Discussion

6.3.1. Flame propagation behavior (Model-A)

Table 6.2 shows the experimental results of the core segregation model (Model-A). All the samples ignited in the range between 203°C and 220°C. Figure 6.3 plots the temperature distribution in the radial direction in terms of the elapsed time. This indicates that the temperature of the center very quickly rises up; within 12 seconds, the temperature rose up from 200°C to 550°C. The thermal conductivity of asphalt is so low that heat flow did not propagate, and the flame was extinguished. Although the core diameter was increased, the flame propagation did not occur. Ignition in the low temperature, NaNO_3 is solid state and the

6. The flame-propagation of the bitumen / nitrate mixture

reaction between ASP and oxidizing agent did not occur. Although the amount of NaNO_3 in the sample was increased, which means that the ratio of the oxidizing agent rise up, the flame propagation did not occurred in case of #A-5. This result means that the flame propagation is not so much dependent on the amount of the oxidizing agent of NaNO_3 . Fraction of NO_3 is range from 39-51wt.%.

At low temperature, though ignition occurred only at the abnormal condition part and the center temperature drastically rose up, the flame propagation may not have occurred.

6.3.2. Flame propagation behavior (Model-B)

Table 6.3 shows the relation between nickel amount and flame propagation behavior. As the amount of $\text{Ni}(\text{NO}_3)_2$ was more than 5.4wt%, the flame propagated all over the sample inside. Under the amount of 5.4 wt% of $\text{Ni}(\text{NO}_3)_2$, ignition occurred only at the center part where AgNO_3 was present, and flame did not propagate outside. The promotion effect of flame propagation containing $\text{Ni}(\text{NO}_3)_2$ may be result from following :

1. Nitric acid is formed because crystal water was decomposed in $\text{Ni}(\text{NO}_3)_2$ and the nitration reaction was proceeded in bitumen / nitrate mixture.
2. The catalyst effects of nickel itself.
3. As $\text{Ni}(\text{NO}_3)_2$ and NaNO_3 coexist, the eutectic was formed and the interface reaction speed between ASP(liquid) and nitrates(liquid) will increase.

In the case of #B-3 sample, flame did not completely propagate, because thermocouples of 15ch. were only inserted in this sample and the heat balance was not the same as in other samples. The molecular weight (ebullioscopes) of asphalt was 1260. The lower limit of $\text{Ni}(\text{NO}_3)_2$ was 5.4wt.%. In this condition, ASP and $-\text{NO}_3$ react with each other and some explosive compounds are formed. (ASP: $-\text{NO}_3 = 1.2: 1.4$) In the sample #B-1 on Fig. 6.4, the burning velocity was measured at 0.23 to 0.92 [mm/s]. The flame temperature ranged from 550°C to 800°C ($\text{ASP} + \text{NaNO}_3 + \text{Ni}(\text{NO}_3)_2$). The flame propagation in the 10 cm diameter of the sample vessel is finished in 100 s.

Figure 6.6 shows the 3d-diagram of the temperature distribution as a function of the elapsed time. The xy-plane indicates the position of the sample inside. The z-plane indicates the temperature corresponding to the passed time. The temperature increased from 200 °C to 750 °C within 9.3 s in the segregation part of AgNO_3 . This result shows the 2 cm center of the

sample. The ignition and combustion occurred very quickly in the center part. In this case, however, the flame propagation did not occur at the outer part, because a lot of thermocouples were inserted in the sample through which the heat was escaped.

The burning velocity of the inner part was lower than that of the outside part. It is found in both cases (Model A and Model B) that even a very few amount of AgNO_3 works as strong igniter.

6.3.3. Infrared Spectrum

Figure 6.8 shows the FT-IR spectrum from 400 to 4000 cm^{-1} . The ordinate indicates transmittance %. All the spectra have absorbance peaks at $3400\text{--}3500\text{ cm}^{-1}$ and 1640 cm^{-1} . The broad peak appearing at $3400\text{--}3500\text{ cm}^{-1}$ is due to the O-H stretching vibration of water and the other peak near 1640 cm^{-1} due to the H-O-H bending vibration.

As the sample (a) and sample (c), C-H stretching vibration was observed at 2924 and 2850 cm^{-1} . In the sample (d) there is no C-H stretching vibration. This result indicates that hydrocarbon and aromatic compounds completely burned out in burned asp.

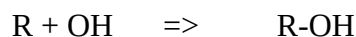
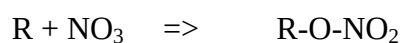
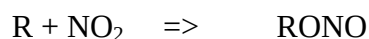
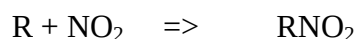
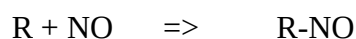
In the samples (b) and (d) containing water, CO_2 was absorbed in the water; thus the spectra of (b) and (c) have strong absorption peaks at 2360 cm^{-1} and 667 cm^{-1} because of CO_2 contaminated from the air atmosphere and burned gas.

The sample (c) (ASP + Metal – Nitrates) has new peaks of 2435 , 2095 , 1788 and 835 cm^{-1} resulting from the reaction between ASP and metal nitrates. In the range from 1300 to 1400 cm^{-1} , the strong absorption peaks presumably result from nitrate compounds. The sample (c) was prepared for methanol stripping. Inorganic metal nitrates cannot dissolve so much in methanol. Some amount of inorganic, metal nitrates could be stripped out. It cannot be concluded whether these absorption peaks result from $-\text{NO}_3$ bounded to aromatic compounds or from inorganic nitrates. It is known that NO stretching frequency varies over a wide range ($24000\text{--}1000\text{ cm}^{-1}$) depending on the bond order. Therefore a narrow frequency range cannot be assigned to the NO group. The yield of the oxidation processes resulting in the formation of carbonyl compounds is much higher than that of the nitration process. The peak at 1788 cm^{-1} indicates C=O stretching vibration. This indicates that samples (a) and (b) react with each other and C=O structure was generated. The C=O stretching vibration indicates that oxidation, nitration and hydration may have occur in the mixture of ASP and nitrates. The sample (c) indicates a strong adsorption at 835 cm^{-1} . This peak seems to be due

6. The flame-propagation of the bitumen / nitrate mixture

to the C-H out-of-plane bending mode. It seems that the asphalt has a catalytic cracking process and thermal cracking process. The molecules broke apart and rearranged to smaller ones. The asphalt is polycyclic aromatic compound. Aromatic compounds of the lighter weight are formed, which may shift the C-H out-of-plane bending mode higher. McMurry[3] pointed out the absorption range between 810 and 850 cm^{-1} is due to *m*-two-substituted aromatic compound or *p*-two-substituted aromatic compound. Other new peaks at 2435 and 2095 cm^{-1} cannot be assigned, whereas there is a possibility of N-H vibration mode of $-\text{C}=\text{NH}^+$ structure.

As C=O bonding is clarified in bitumen / nitrate mixture using FT-IR, this result suggests a lot of chemical reactions occurred in the sample. In the mixture of ASP + Metal – Nitrates, nitration, oxidation and esterification reactions may have took place according to the following:



Nowak[4] has reported that the yields of the oxidation processes resulting in the formation of carbonyl compounds are much higher than those of the nitration processes in case of TBP- HNO_3 - H_2O systems. TBP and ASP are organic materials and the molecular weights of them are so large and similar reactions may have occurred.

6.4. Conclusion

When $\text{Ni}(\text{NO}_3)_2$ was segregated at the center part of the sample, ignition occurred only at the center and the flame did not propagate to other parts. However, flame propagation occurred in the case that $\text{Ni}(\text{NO}_3)_2$ was present more than 5.4 wt% in the dispersed condition. The speed of the flame propagation was measured at 0.23 to 0.92 [mm/s]. The amount of the nickel nitrate affected the speed of the flame propagation. At the part where AgNO_3 was

6. The flame-propagation of the bitumen / nitrate mixture

present, bitumen / nitrate mixtures ignited about 220 °C and the ignition behavior was very quick; the flame temperature was up to 800 °C in 7 s. From the results of FT-IR analysis, the nitration of the mixture of ASP and nitrate salts may be occurred.

Under the abnormal condition resulting from thermal storage and segregation of metal nitrates such as AgNO_3 without $\text{Ni(NO}_3)_2$, the flame did not easily propagate in spite that the usual chain reaction occurred when the bituminized products ignited. On the other hand, in the case that $\text{Ni(NO}_3)_2$ was in the dispersed condition, the flame easily propagated.

6. The flame-propagation of the bitumen / nitrate mixture

Table 6. 1 Bituminization facility and some accidents in the world.

Country	Facility	Source of waste	Process type	Type of asphalt	Accident
Belgium	Mol	Various waste	Batch	Strate	-
		Reprocessing	Extruder	Blown	Dec,1981 / Firing
England	Harwell	Various waste	Batch	Strate	-
France	La Hague	Reprocessing	Extruder	Strate	-
	Marcoule	Reprocessing	Extruder	Strate	-
	Saclay	Various waste	Thin layer distillation	Strate	Aug,1977 / Firing, Oct,1992 / Firing
German	Karkruhe	Various waste	Extruder	Blown	Apr,1974 / Firing
Japan	Tokai	Reprocessing	Extruder	Blown	March,1997 / Fire and Explosion
Sweden	Barseback	Nuclear power plant	Thin layer distillation	Strate	-
	Forsmark-1.-2	Nuclear power plant	Batch	Strate	-
	Forsmark-3	Nuclear power plant	Batch	Strate	-
Switzerland	Goesgen	Nuclear power plant	Extruder	Strate	-
USSR		Nuclear power plant	Thin layer distillation	Blown / Strate	-

6. The flame-propagation of the bitumen / nitrate mixture

Table 6. 2 Experimental results of Model-A.

Sample No.	Bulk component			Core component		Diameter [cm]	H.R. [°C/min]*1	SIT [°C]	H.T. [°C]*2	Result *3
	ASP [g]	NaNO ₃ [g]	Fraction of NO ₃ [wt.%]	Mixture weight [g]	AgNO ₃ [g]					
#A-1	150	60	39%	3	3	1.2	1	213	292	-
#A-2	150	60	39%	8	2	2.0	1	203	553	-
#A-3	150	60	39%	20	2	3.1	1	205	312	-
#A-4	150	60	39%	20	1	3.1	2	220	533	-
#A-5	150	90	51%	20	2	2.9	1	185	212	-

*1 H.R.=Heating rate

*2 H.T.=Highest temperature

*3 + :Flame propagation

- :Not Flame propagation

Table 6. 3 Experimental results of Model-B.

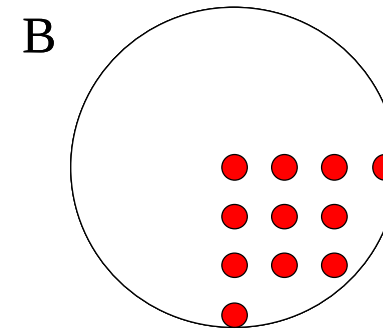
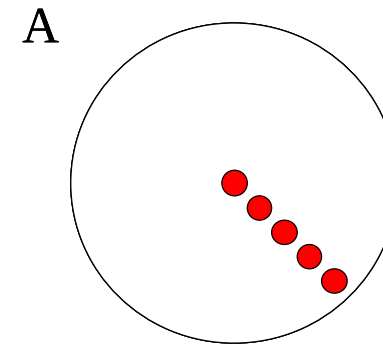
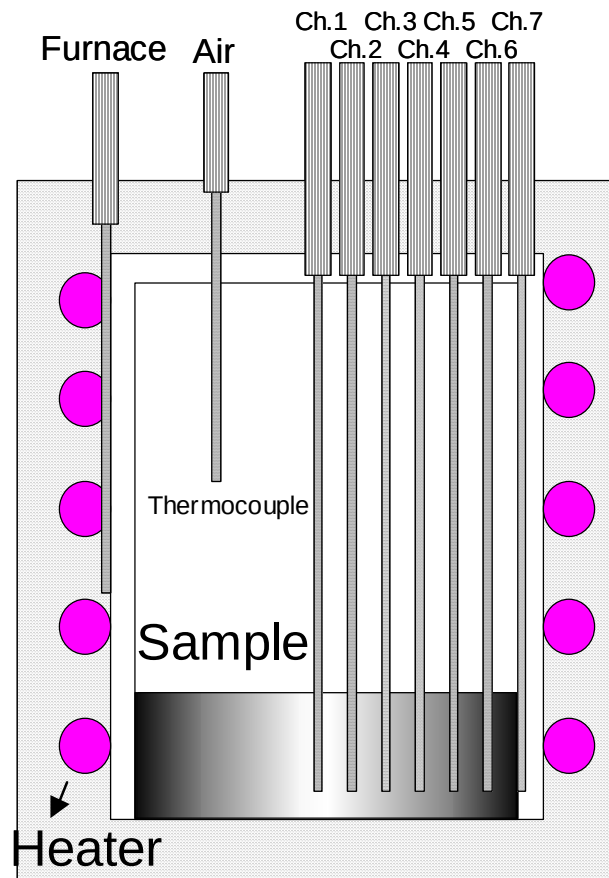
Sample No.	Sample component				Fraction of Ni(NO ₃) ₂ [wt.%]	Fraction of NO ₃ [wt.%]	H.R. [°C/min]*1	SIT [°C]	Result*2
	ASP [g]	NaNO ₃ [g]	Ni(NO ₃) ₂ ·6H ₂ O [g]	AgNO ₃ [g]					
#B-1	150	60	30	2	7.8%	23.6%	1	210	+
#B-2	150	60	30	7.8	7.6%	23.6%	1	225	+
#B-3	150	60	20	1	5.4%	22.7%	1	229	+
#B-4	150	60	20	2	5.4%	22.7%	1	220	+
#B-5	150	60	20	2	5.4%	22.7%	1	211	+
#B-6	150	60	15	1	4.2%	22.3%	1	228	-
#B-7	150	60	10	1	2.8%	21.8%	1	211	-

*1 H.R.=Heating rate

*2 + :Flame propagation

- :Not Flame propagation

6. The flame-propagation of the bitumen / nitrate mixture



Distribution of the thermocouple
in the sample:view top

Figure 6. 1 Heating apparatus and disposition of the thermocouples.

6. The flame-propagation of the bitumen / nitrate mixture

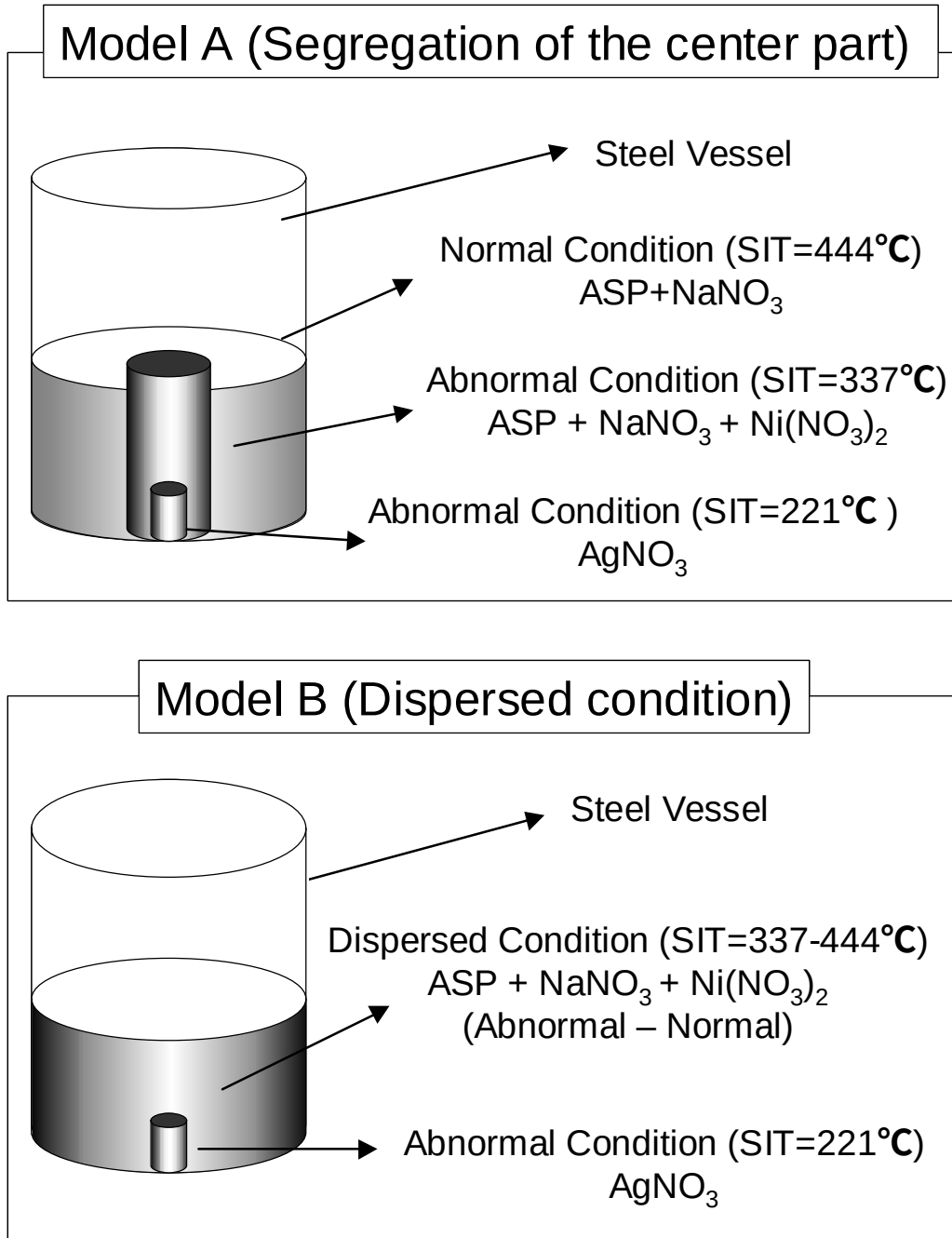


Figure 6. 2 Two possible models of the burnable bituminized products at low temperature

6. The flame-propagation of the bitumen / nitrate mixture

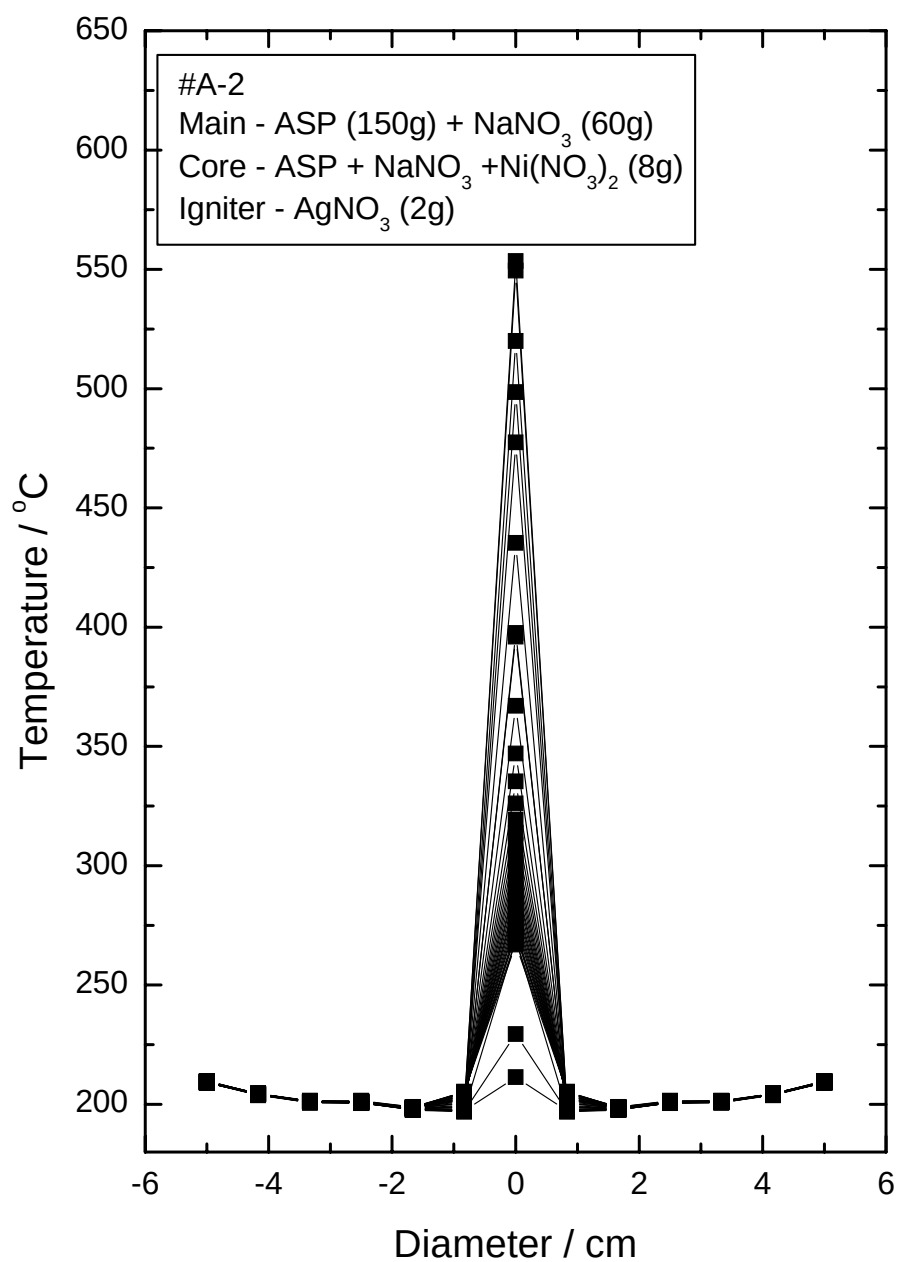


Figure 6. 3 Temperature distribution in the radial direction (Model A).

6. The flame-propagation of the bitumen / nitrate mixture

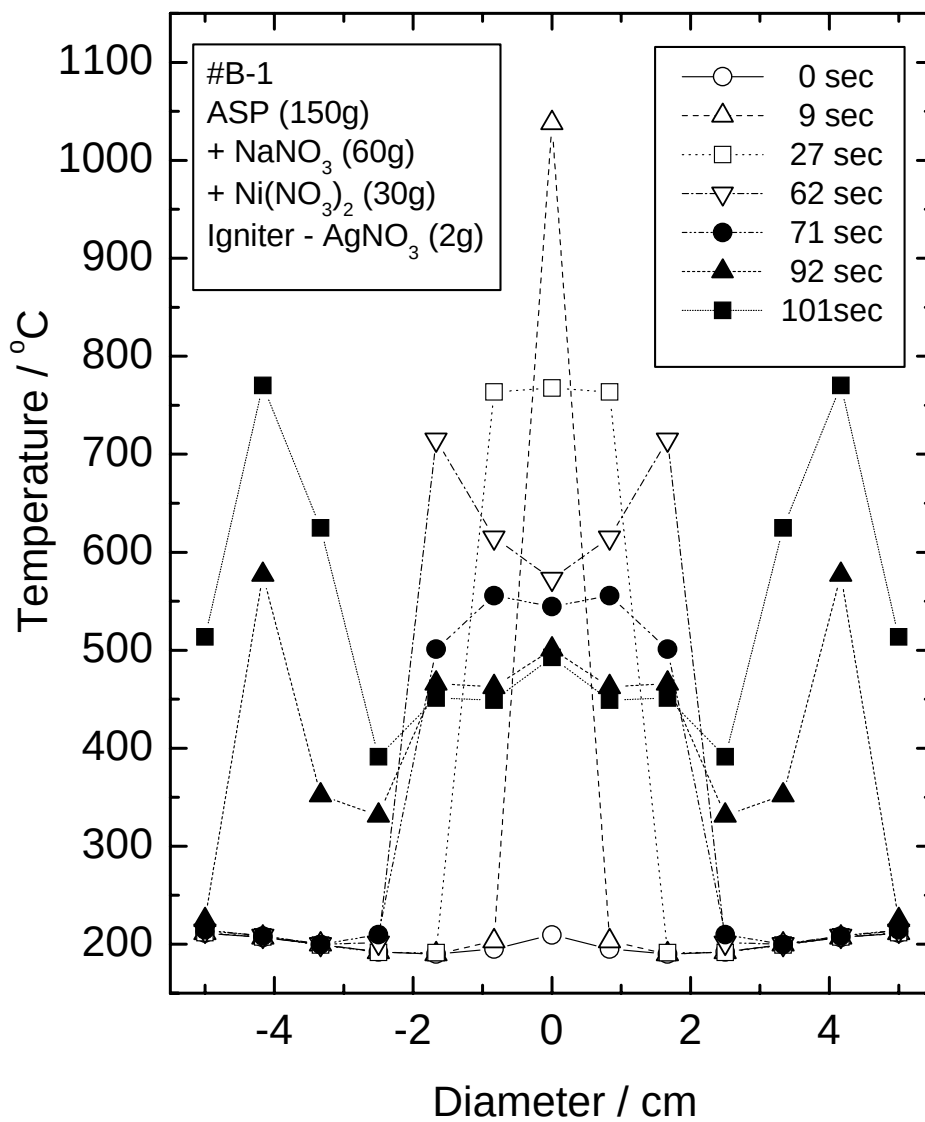


Figure 6. 4 Temperature distribution in the radial direction (Model B)

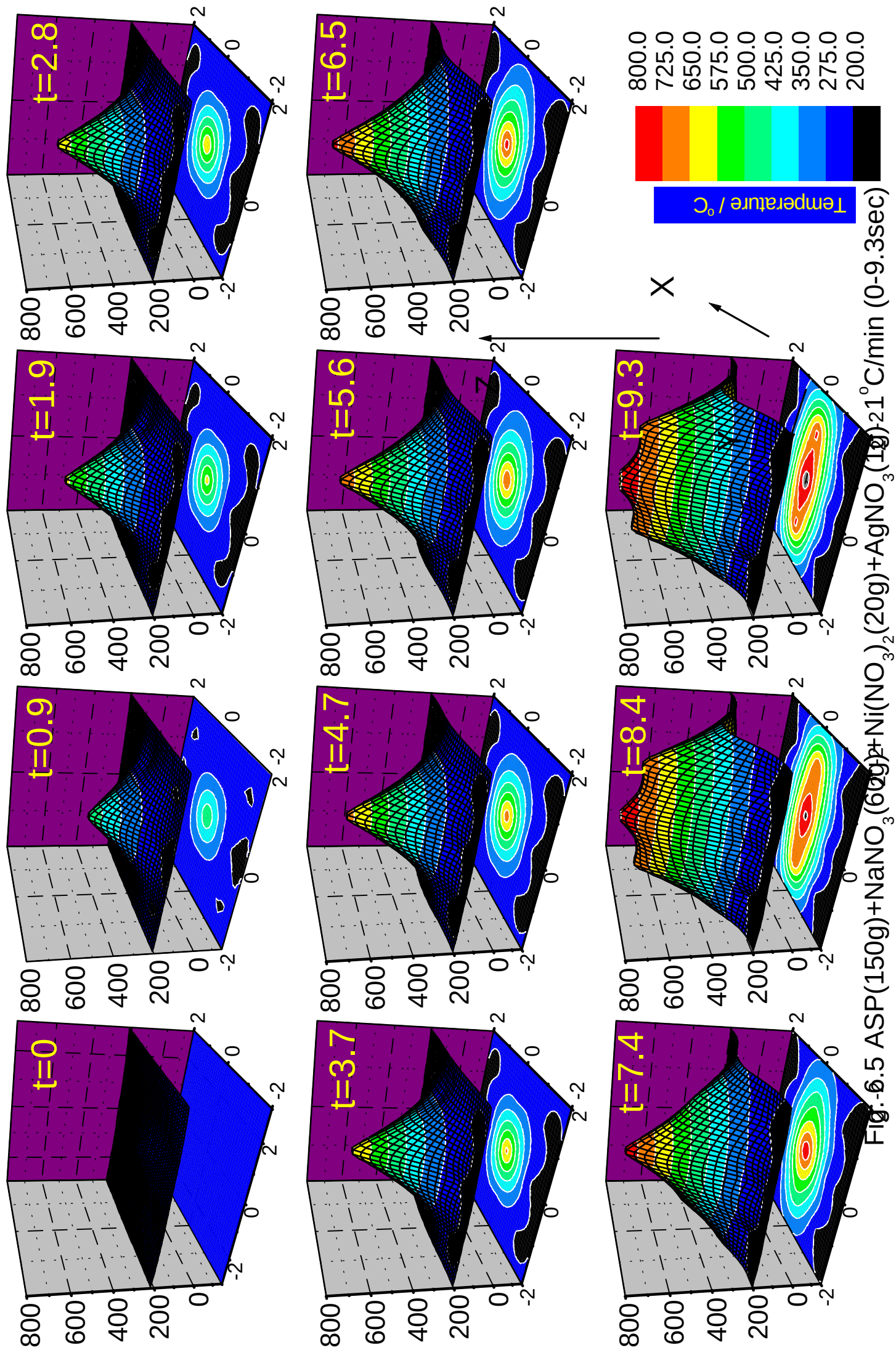
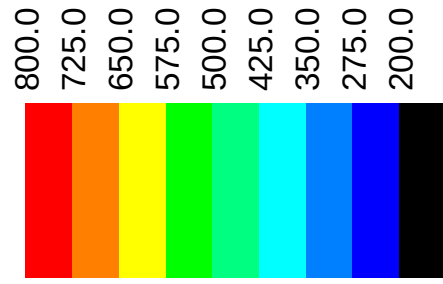


Fig. 6.5 ASP(150g)+ NaNO_3 (60g)+ $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (20g)+ AgNO_3 (10g) $21^{\circ}\text{C}/\text{min}$ (0-9.3sec)



X

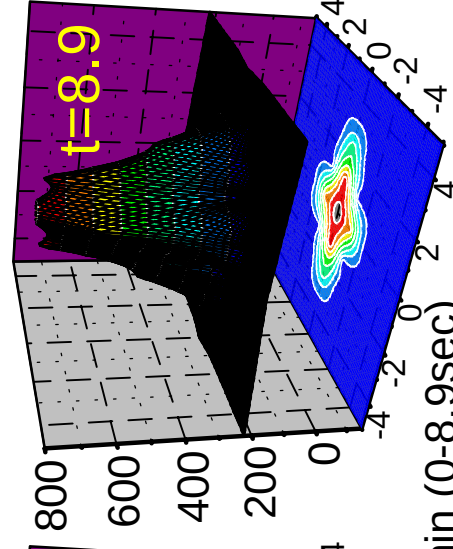
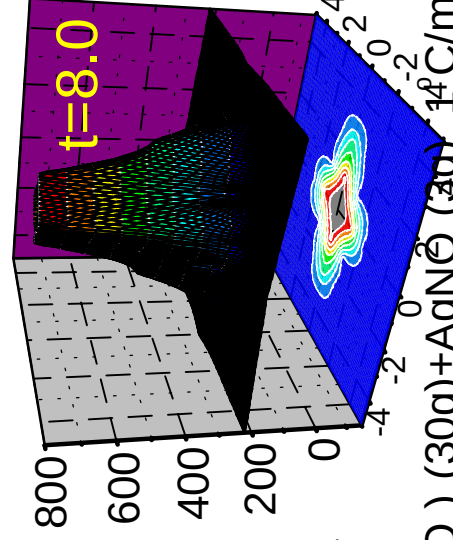
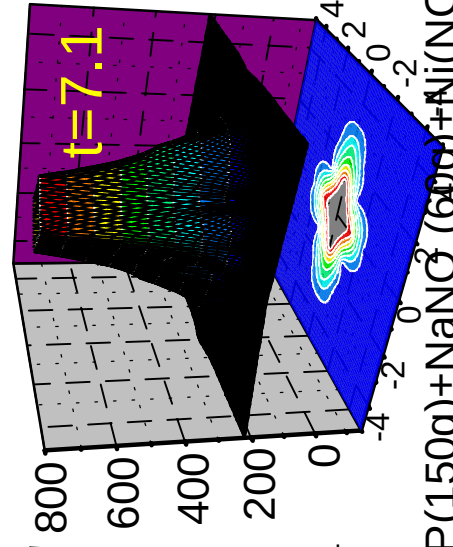
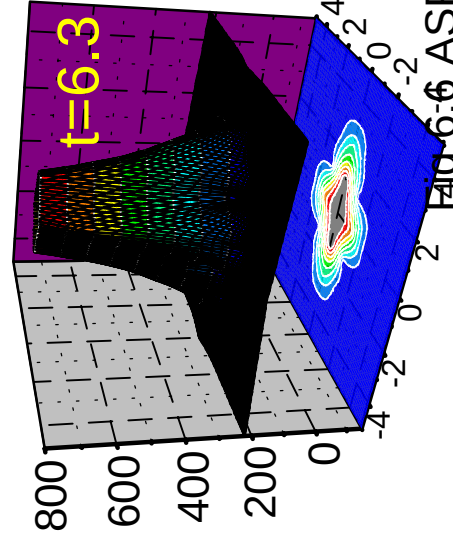
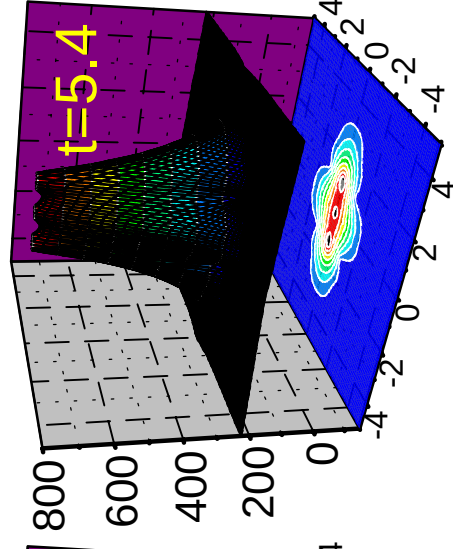
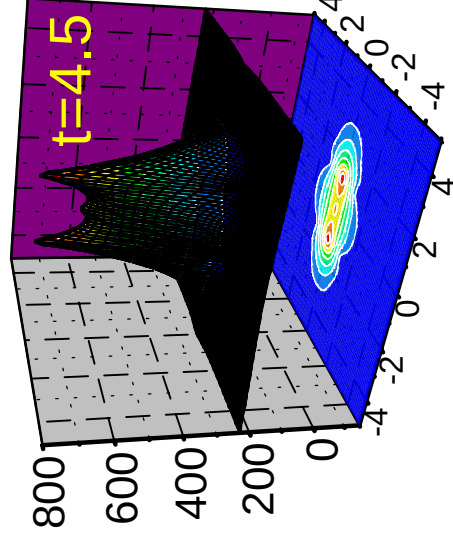
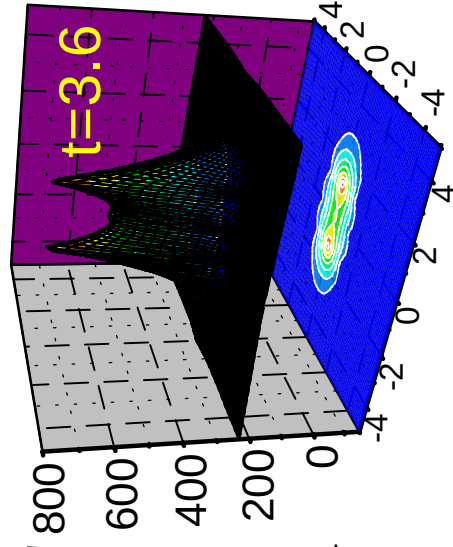
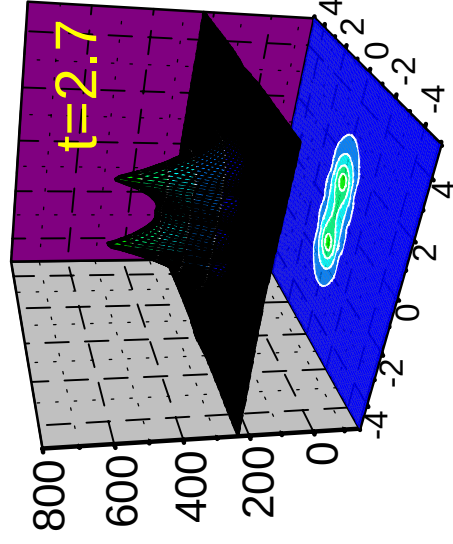
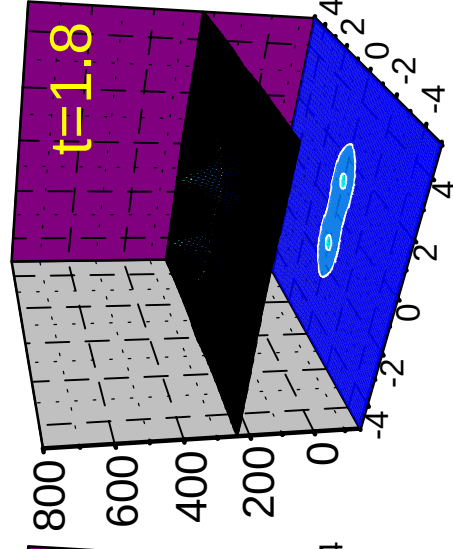
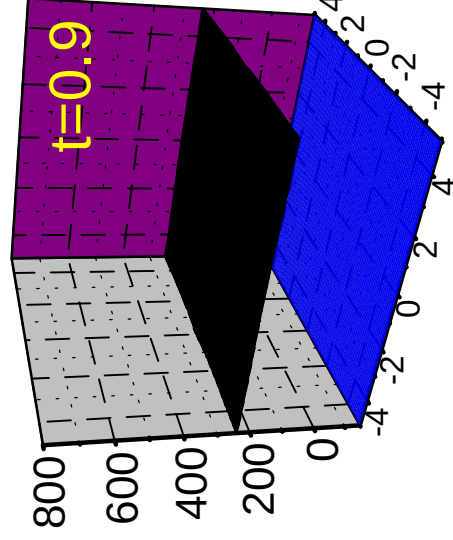
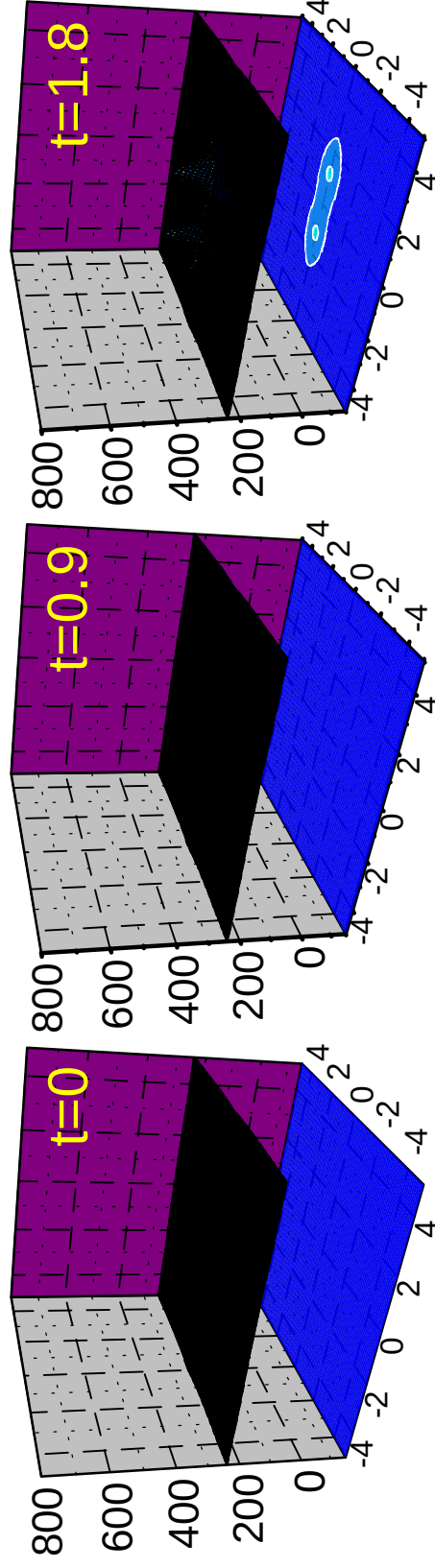
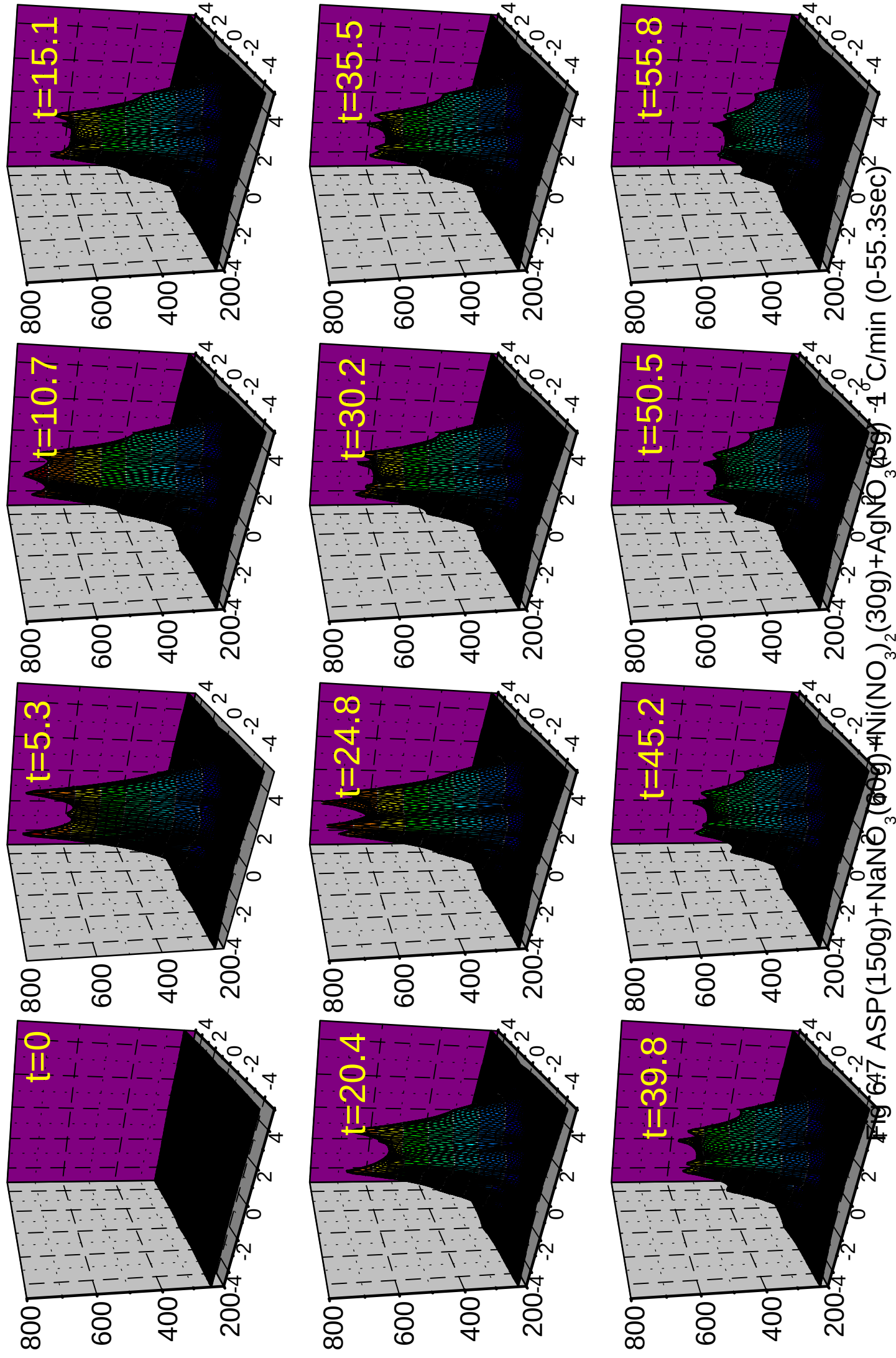


Fig. 6-6 ASP(150g)+NaNO₃(60g)+Ni(NO₃)₂(30g)+AgNO₃(2g) 14°C/min (0-8.9sec)



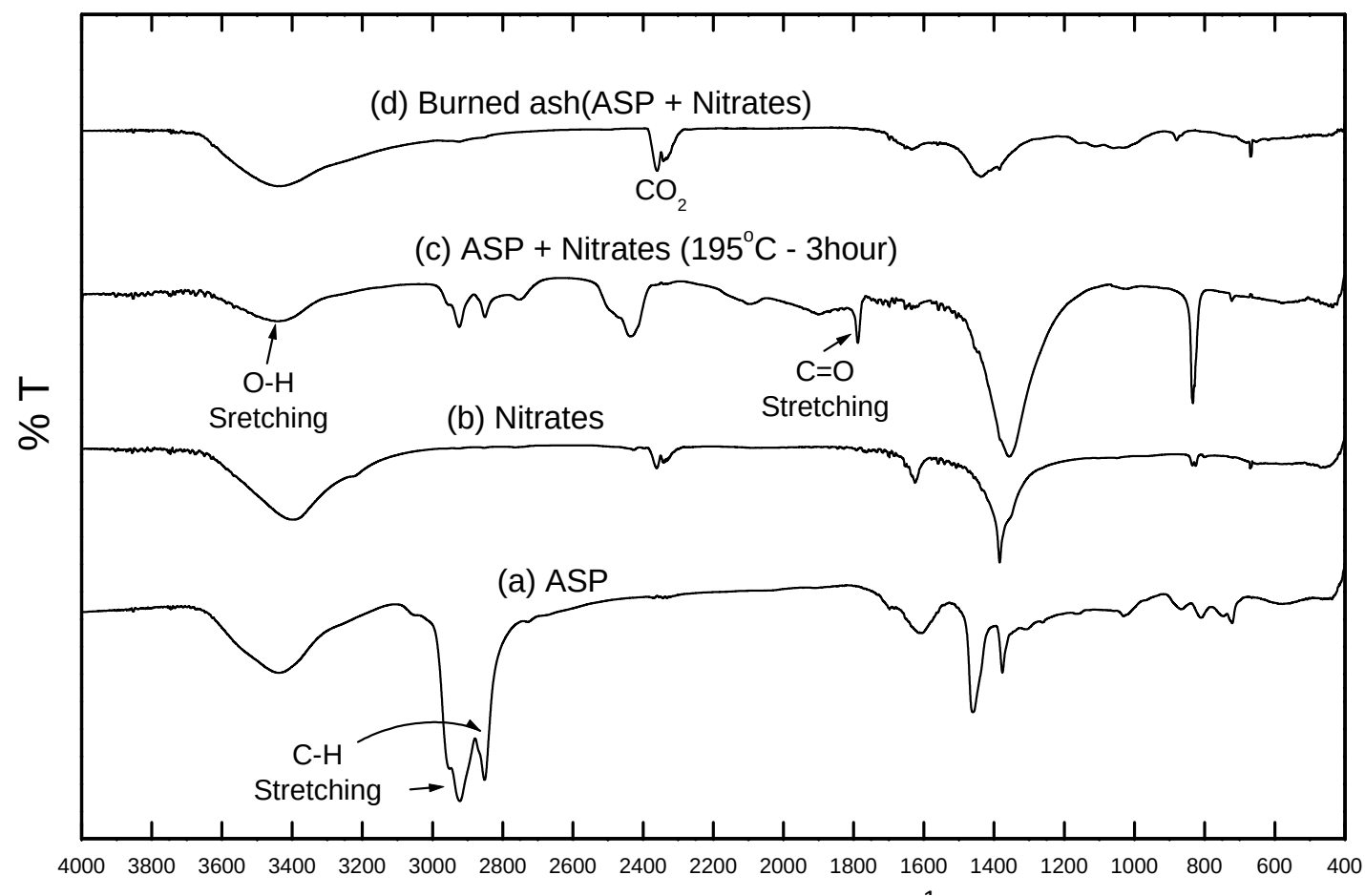


Figure 6. 8 IR spectrum of ASP (a), metal – nitrates (b), ASP + metal – nitrates (c) and Burned ash (d),

in the range from 400 cm^{-1} to 4000 cm^{-1}

6. The flame-propagation of the bitumen / nitrate mixture

References

- [1] Technical Report Series No. 352 Bituminization processes to condition radioactive wastes, IAEA VIENNA, 1993.
- [2] Technical Report Series No. 116 Bituminization of radioactive wastes, IAEA VIENNA, 1970.
- [3] John McMurry, Organic Chemistry 3rd. Ed., Brooks/Cole, 1992.
- [4] Zofia Nowak, Radiolytic degradation of extractant-diluent system used in the purex process, Nukleonika, Vol.22, 1976.

7. Conclusions

The present work does not point out the direct cause of the accident but the potential hazard of the bituminization process. The bituminization in reprocessing will not be used again in Japan. The importance is that we should accumulate the information about the accident and the accident should be avoided. Especially, the bituminized product is a mixture of organic compounds and nitrates. The accident analysis is helpful for prevention of red oil accidents. The red oil hazard is a problem for reprocessing and a lot of accidents have been reported. The commercial based PUREX reprocessing plant in Rokkasyo village will start up at 2005 and the information about hazardous chemical reactions should be accumulated. Here, we conclude this thesis.

In Chapter 1, the background of the present study is stated.

In Chapter 2, some serious accidents, which occurred in the nuclear reprocessing plants in the world, are reviewed.

In Chapter 3, a new method of thermal analysis is presented.

In Chapter 4, it is stated that the SIT of bitumen + NaNO_3 is higher than 450°C . However, if the sample contains the nickel, the SIT decreases as low as to 330°C . Moreover, if the sample contains Ag and Ni, the ignition temperature drastically decreases to 200°C . Fe(III) works as oxidant in the bitumen and the viscosity of asphalt increases and it is possible that the friction heat can occur in the extruder. This result does not necessarily point out the direct cause of the accident at Tokai Bituminization Demonstration Facility but presumably general hazardous chemical reactions between organic and nitrates in reprocessing.

In Chapter 5, the results are stated for the experiments where the mixture of ASP, NaNO_3 , $\text{Ni}(\text{NO}_3)_2$ and AgNO_3 or AgI were heated at the rate between 0.5 and $4.0^\circ\text{C}/\text{min}$. The SIT of bitumen mixtures involving AgNO_3 is dependent on the heating rate. In contrast, the SIT of bitumen mixtures involving AgI is independent of the heating rate. The activation energy E_a for the ignition of bitumen / nitrate mixtures has been calculated at 30 kJ/mol .

Therefore, silver fulminate is assumed to be the initiator of the self-ignition of the bitumen nitrate mixture involving AgNO_3 .

In Chapter 6, the case is mentioned in which flame propagates, if $\text{Ni}(\text{NO}_3)_2$ is present in more than 5.4 wt% in dispersed condition. The speed of the flame propagation is determined to be between 0.23 and 0.92 [mm/s]. In the abnormal phenomena resulting from thermal storage and segregation of metal nitrates, flame does not propagation even if the part of the bituminized products ignites and the chain reaction at the normal condition of the bituminized products may not readily occur. On the other hand, if $\text{Ni}(\text{NO}_3)_2$ exists in dispersed condition, the flame propagation may easily occur.

It is pointed out that in the nuclear fuel reprocessing using organic solvents and nitric acid, the coexistence of organic waste and Ag, Ni and Fe ions would cause generation of ignitable complex materials.

Appendix

1, Possible classes of explosive compounds in SRS Waste constituents

High-level nuclear waste is stored at the SRS in a highly alkaline form in underground carbon steel tanks. Because of the high pH, the waste consists of two phases, a liquid phase or supernate.

Fourteen classes of explosive compounds were identified as conceivably being present by comparing the list of known elements and species in current or planned chemical processing operations with explosive compounds and reactions listed in the literature [1]. A list of the fourteen classes of compounds is given in Appendix 1. A comprehensive list of conceivable explosive compounds is provided in Appendix 2.

2, Preparation methods of silver fulminate

6.8g silver nitrate were dissolved in 4ml water and 20ml nitric acid were added. 36ml ethanol were added and mixture heated to 40°C in a water bath. The temperature rose to 62°C over twenty minutes and the reaction was allowed to proceed for a further 30 minutes, the temperature rising to 68°C and subsequently falling to 43°C at which point 100ml water were added. The precipitation of fine needles was filtered off, washed with water and dried on a steam table. The yield obtained was 4.5g (75% of theoretical). It is white crystalline material which darkens on exposure to light, non-hygroscopic, only slightly soluble in water (0.075g in 100ml at 13 °C / 0.25 g in 100ml at 100 °C), insoluble in nitric acid and in decomposed by hydrochloric acid. IR spectrum measured and the spectrum was shown in Appendix 3.

3, Ignition temperature of AgCNO

Normally, there are two types of ignition temperature test.

- (a) Ignition temperature is measured when it is heated at constant heating rate.
- (b) An elapsed time is measured until the sample ignites when the sample is heated at constant temperature.

Here is a different point of these methods (a) and (b).

(a) Constant heating speed test

Procedure

1. 0.1g of samples are introduced to test tube b, which is 15mm inner diameter, 0.5mm thickness and 125mm length. The test tube is sealed by the cork and 45mm of the test tube is heated at 100°C by the oil bath a.
2. The temperature meter c is inserted to the empty test tube and the height of the temperature meter is set as that of the samples.
3. The temperature of oil bath is raised at 5°C/min and the ignition temperature is measured. When it ignites, the cork is blown off and it crumpled out.

(b) Constant temperature test

1. The thermometer is inserted to the temperature measurement hole of crucible. In the case of thermocouple, the top of the thermocouple should be touched with the bottom of the hole.
2. The temperature of the apparatus is kept in the range from 200 to 400°C, after that the cooling rate is adjusted to 2°C/min.
3. The sample is separated on the cup about 20mg.
4. When the temperature go down 10°C lower than the adjusted temperature, the sample is introduced to the crucible at once. The waiting time (θ [s]) of ignition is measured every 5°C decrease.
5. When the waiting time of ignition is over 1min, the test should be stopped.
6. After the relation between $\log \theta = A/T - B$ is determined, the ignition temperature is defined when the waiting time of ignition is range from 4 to 5 sec.

Table Ignition test of fulminates

Materials	Ignition temperature	Testing method	about	reference
Hg(CNO) ₂	170-180°C	Constant heating speed test		[2]
AgCNO	169-175°C	Constant heating speed test	heating rate = 20°C/min	[3]
AgCNO(precipitated)	220°C	Constant temperature test	waiting time of ignition=4.3sec	[4]
AgCNO(crystalline)	220°C	Constant temperature test	waiting time of ignition=4.6sec	[4]
AgCNO(commercial)	202-204°C	unknown		[5]
AgCNO(prepared)	224-228°C	unknown		[5]
AgCNO	170°C	unknown		[5]
Hg(CNO) ₂	210°C	unknown		[6]
AgCNO	208°C	Constant temperature test	heating rate=0.5°C/min	This work

Appendix 1 Conceivable explosive compound classes in SRS waste tanks

Known to exist but controlled

- Flammable gases
- Metal nitrides
- Ammonia compounds and derivatives

Possible and need additional study

- Metal NO_x compounds
- Organics

Not possible

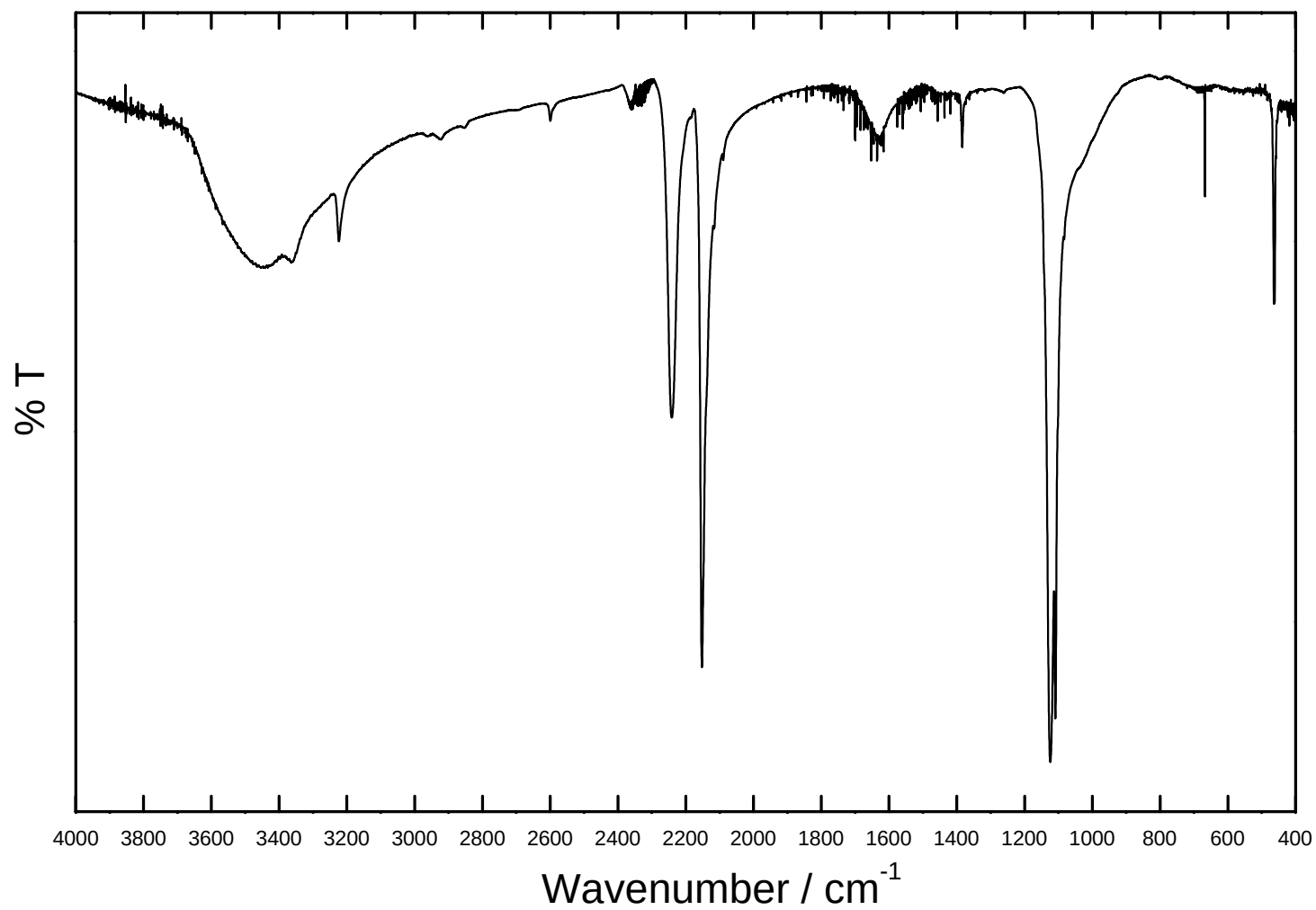
- Metal fulminates
- Metal azides
- Halogen compounds
- Metal-amine complexes
- Nitrate/oxalate mixtures
- Metal oxalates
- Metal oxohalogenates
- Metal cyanides/cyanates
- Peroxides

Appendix 2 Comprehensive Listing of Conceivable Explosive Compounds
in SRS waste tank farm facilities (page1 of 3)

Compound	Formula
Barium hexanitride	BaN_4
Barium peroxide	BaO_2
Calcium peroxide	CaO_2
Chloride heptaoxide	Cl_2O_7
Chloride oxide	ClO_2
Hexaamminechromium(III) nitrate	$[(\text{H}_3\text{N})_6\text{Cr}](\text{NO}_3)_3$
Pentamminenitratochromium(III) nitrate	$[(\text{H}_3\text{N})_3\text{Cr}(\text{NO}_3)](\text{NO}_3)_2$
Diamminenitratocobalt(II) nitrate	$[(\text{H}_3\text{N})_2\text{Co}(\text{NO}_3)](\text{NO}_3)$
Tramminetrinitrocobalt	$(\text{H}_3\text{N})_3\text{Co}(\text{NO}_3)_3$
Trihydrazinecobalt(II) nitrate	$[(\text{H}_4\text{N}_2)_3\text{Co}](\text{NO}_3)_3$
Ammonium hexanitrocobate	$(\text{H}_4\text{N}^+)_3[\text{Co}(\text{NO}_3)_6]^{-3}$
Pentaamminenitratocobalt(III) nitrate	$[(\text{H}_3\text{N})_6\text{Co}(\text{NO}_3)](\text{NO}_3)_2$
Hexamminecobalt(III) permanganate	$[(\text{H}_3\text{N})_6\text{Co}](\text{MnO}_4)_3$
Hexahydroxyamminecobalt(III) nitrate	$[(\text{HONH}_2)_6\text{Co}](\text{NO}_3)_3$
Hexamminecobalt(III)	$[(\text{H}_3\text{N})_6\text{Co}][\text{Co}(\text{NO}_3)_6]$
Hexanitratocobaltate(III)	
Teraammine copper(II) nitrite	$(\text{H}_3\text{N})_4\text{Cu}(\text{NO}_2)_2$
Teraammine copper(II) nitrate	$(\text{H}_3\text{N})_4\text{Cu}(\text{NO}_3)_2$
Teraammine copper(II) sulfate	$(\text{H}_3\text{N})_4\text{CuSO}_4$
Cuprous azide	CuN_3
Cupric azide	$\text{Cu}(\text{N}_3)_2$
Tetraammine copper(II) azide	$(\text{H}_3\text{N})_4\text{Cu}(\text{N}_3)_2$
Lead Chorite	PbIO_2
Lead Tetrachloride	PbCl_4
Lead hyponitrite	PbN_2O_2
Manganese oxide	MnO_2
Potassium permanganate	$\text{K}_2\text{Mn}_2\text{O}_7$
Potassium peroxide	K_2O_2

Compound	Formula
Mercuric fulminate	$\text{Hg}(\text{CNO})_2$
Mercuric nitride	Hg_3N_2
Mercuric oxalate	$\text{Hg}_2\text{C}_2\text{O}_4$
Mercuric oxycyanide	$\text{Hg}(\text{CN})_2\text{HgO}$
Mercuric chlorate	HgClO_3
Mercuric nitrate	HgNO_3
Mercuric nitride	HgN_3
Mercuric peroxide	HgO_2
Nitrobenzene	$\text{C}_6\text{H}_5\text{NO}_2$
1,3,5-trinitrobenzene	$\text{C}_6\text{H}_3\text{N}_3\text{O}_6$
2-nitrophenol	$\text{C}_6\text{H}_5\text{NO}_3$
4-nitrophenol	$\text{C}_6\text{H}_5\text{NO}_3$
2,4-dinitrophenol	$\text{C}_6\text{H}_2\text{N}_3\text{O}_7$
2,4,6-trinitrophenol	$\text{C}_6\text{H}_2\text{N}_3\text{O}_7$
1,2-dinitrobenzene	$\text{C}_6\text{H}_4\text{N}_2\text{O}_4$
1,3- dinitrobenzene	$\text{C}_6\text{H}_4\text{N}_2\text{O}_4$
2-nitroaniline	$\text{C}_6\text{H}_6\text{N}_2\text{O}_2$
3-nitroaniline	$\text{C}_6\text{H}_6\text{N}_2\text{O}_2$
4-nitroanile	$\text{C}_6\text{H}_6\text{N}_2\text{O}_2$
Diamminepalladium(II) nitrite	$(\text{H}_3\text{N})_2\text{Pd}(\text{NO}_2)_2$
Diamminepalladium(II) nitrate	$(\text{H}_3\text{N})_2\text{Pd}(\text{NO}_3)_2$
<i>cis</i> -Diammineplatinum(II) nitrate	$(\text{H}_3\text{N})_2\text{Pt}(\text{NO}_3)_2$
Selenium nitride	SeN_4
Silicon diiodide	SiI_2
Sodium peroxide	Na_2O_2
Strontium peroxide	SrO_2
Didydrazine tin chloride	$(\text{H}_4\text{N}_2)_2\text{SnCl}_2$

Compound	Formula
Zinc peroxide	ZnO_2
Dihydroxyammine zinc chloride	$(\text{HONH}_2)_2\text{ZnCl}_2$
Nitrogen trichloride	NCl_3
Nitrogen triiodide	NI_3
Ammonia nitrogen triiodide	NH_3NI_3
Hydroxylamine	HONH_2
Hydroxylamine nitrate	$\text{NH}_2\text{OH}.\text{HNO}_3$
Ammonium nitrite	NH_4NO_2
Ammonium nitrate	NH_4NO_3
Ammonia iodate	NH_4IO_3
Ammonia chlorate	NH_4ClO_3
Ammonum perchlorate	NH_4ClO_3
Hydrazine	N_2H_4
Hydrazinium nitrate	$\text{N}_2\text{H}_4\text{HNO}_3$
Hydrogen Azide	HN_3
Hyponitrousd Acid	$\text{H}_2\text{N}_2\text{O}_2$
Hydrogen Peroxide	H_2O_2
Silver oxalate	$\text{Ag}_2\text{C}_2\text{O}_4$
Silver azide	AgN_3
Silver nitride	Ag_3N
Silver amide	AgNH_2
Silver azide chloride	AgClN_3
Silver perchlorate	AgClO_4
Silver chlorate	AgClO_3
Silver chlorite	AgClO_2
Hydrazine silver nitrate	$(\text{H}_4\text{N}_2)\text{AgNO}_3$
Silver iodate	AgIO_3
Silver peroxide	Ag_2O_3
Silver fulminate	$\text{Ag}(\text{CNO})$
Silver hyponitrite	$\text{Ag}_2\text{N}_2\text{O}_2$
Diammine silver permanaganate	$(\text{H}_3\text{N})_2\text{AgMnO}_4$



Appendix 3 Infrared Spectrum of silver fulminate (AgCNO)

Reference

- [1]. P G Urban and Akzo-Nobel (Eds.), Bretherick's Handbook of Reactive Chemical Hazards 6th ed., Butterworth, London (1999).
- [1] Kayaku gakkai regulations(IV), Kayaku gakkai.
- [2] K.K. Andreev, Explosivstoffe 10,229-237(1962)
- [3] Kartar Singh, Sensitivity of cuprous azide towards heat and impact, Trans. Faraday Soc.,55,124-129(1958)
- [4] P.H.Collins and K.J.Holloway, A reappraisal of silver fulminate as a detonant, Propellants and Explosives 3, 159-162(1978)
- [5] Rosenberg, Chem Ztg 37, 933(1913)

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