Fire at Notre Dame Cathedral and Lead Materials in the Environment

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ABSTRACT

This literature review deals with lead materials in fire and related environmental issues based on inorganic chemistry. In 2019, the Notre Dame Cathedral fire raised not only the issue of damage to historical building, but also the issue of the impact of lead materials on the environment as well as human health. Three months after the fire, French media reported that lead contamination had been detected in the area around the cathedral, with lead levels 500-800 times higher than the safety requirements. More than 200 tons of lead used in the roofs and spire melted in the fire. Besides this French fire case, chemical aspects of lead (element and compounds), usage of lead as building materials (Japanese castle, paint for a highway bridge, and protection against radioactive rays) on past architectural fires, energy materials (gasoline, lead-acid battery, and Perovskites solar cells in future) and their potential fire risk, and impact to human are also reviewed in this paper.

Keywords: Fire, Lead, Notre Dame Cathedral, Building Materials, Energy Materials

1. INTRODUCTION

1.1 Fire at Notre Dame Cathedral in 2019

The April 15, 2019 fire at Notre Dame Cathedral in Paris, France shocked the citizens of Paris as well as the world. The fire caused the roof and spire of the cathedral to collapse, but the main part of the building remained intact and treasures were removed from the cathedral. President Macron immediately announced that the cathedral would be rebuilt by 2024, the year of the Paris Olympics, and rebuilding work in underway [1, 2].

However, in July 2019, three months after the fire, French media reported that lead contamination had been detected in the area around the cathedral, with lead levels 500-800 times higher than the safety requirements. More than 200 tons of lead used in the roofs and spire melted in the fire [3]. Media reports and warnings from environmental groups raised concerns about lead contamination, so work to rebuild the cathedral was temporarily suspended to ensure the safety of workers, and two schools in the area were closed.
The Notre Dame Cathedral fire raised not only the issue of damage to historical monuments, but also the issue of the impact of lead on the environment and human health. The impacts of lead after the Notre Dame Cathedral fire as published [4], as well as the impacts of lead on past architectural fires in the literature are reviewed in this paper. The literature on lead and fire in energy materials is also reviewed and future issues are presented.

1.2 Issues Raised in the Fire

The condition of the cathedral after the fire was investigated by the French Historical Monuments Research Laboratory (LRMH), the agency responsible for the conservation of French historical monuments, which includes scientists from geology to metallurgy. It not only directs engineers to prevent damage to the cathedral and preserve it, but also investigates lead contamination and recommends decontamination methods. The activities of LRMH and introduced the scientists' research and views on lead contamination [4].

Metallurgists at the LRMH metals division believed that the fire was well below the lead's evaporation temperature of 1700°C, and that most of the lead melted at 300°C. However, in places the temperatures exceeded 600°C, and the lead oxidized into an aerosol. Yellow smoke rose from the cathedral at the time of the fire, indicating that the lead aerosols were carried by air. Geochemists from the French Alternative Energies and Atomic Energy Commission analyzed the isotope characteristics that distinguish the lead collected at the cathedral from other lead to determine how far the smoke reached.

Samples taken from nearby schools showed high lead levels and were decontaminated. But it is not clear whether the lead came from the Notre Dame fire or from some other sources, such as lead paint, car batteries, or lead-containing gasoline, because the agency that originally surveyed the schools destroyed the wipes and it is now impossible to do an isotopic analysis.

France's national health agency imposes legal limit of 0.1 μg per square centimeter of surface of buildings including historical monuments because of toxicity of lead. According to the wood scientist, the first samples from the oak confessional and choir seats showed 70 times higher than the safety requirements.

The blood tests of the scientists have shown no significant rise in their lead levels. Nevertheless, the national work inspection agency has forced strict safety requirements. People entering the cathedral must wear disposable paper underwear and safety suits and must wear a protective mask. The stay is limited to 150 minutes, and after their stay they must take a shower and wash themselves from head to toe.

The French Ministry of Culture has charged LRMH to find a way to cleanse the lead without damaging the cathedral. Scientists from the LRMH glass division tested the decontamination techniques on 113 stained glass windows in the cathedral that remained intact. Examination of three panels under a microscope revealed lead oxide nodules.

The national health agency used commercial wet wipes to sample surfaces and test for lead, but the wipes contained small amounts of acid that could damage the window
staining, so the scientists convinced the agency to use chemical-free baby wipes sold in grocery stores. The scientists were still reluctant to clean the entire cathedral with baby wipes. They found that the lead on smooth surfaces such as glass, metal, waxed wood, and painted surfaces could be removed with a vacuum and a cotton sponge moistened with distilled water. Methods for cleaning porous stones have also been suggested for cleaning lead with as little damage to the cathedral as possible.

As mentioned above, the restoration of Notre Dame Cathedral must proceed with caution due to the issue of lead cleaning.

2. FEATURES OF LEAD

The general characteristics of lead and its applications are described in the following sections.

2.1 Chemical Characteristics of Lead

Lead, atomic number 82, atomic weight 207.20, is a bluish-white or silver-gray lustrous metal that could be oxidized to a lead color (blue-gray) when exposed to air [5]. Lead has a relatively low melting point of 327.4°C, with densities about 1.4 times those of iron, and is easy to work with because of ductility and softness [6]. It is easily oxidized and therefore has excellent corrosion resistance [7].

Lead is an amphoteric element that dissolves in aqueous solutions of nitric acid and strong bases to produce hydrogen, but is almost insoluble in hydrochloric acid and dilute sulfuric acid because it forms an insoluble lead(II) chloride (PbCl₂) and lead(II) sulfate (PbSO₄) film on its surface. Since its ionization tendency is small, it easily reacts with various ions to form precipitates. Three major precipitates of lead(II) ions: lead(II) hydroxide (Pb(OH)₂), PbCl₂, and PbSO₄ are white precipitates, lead(II) sulfide (PbS) is precipitated in black, and lead(II) chromate (PbCrO₄) is precipitated in yellow. PbCl₂ reacts to light and turns grayish-yellow or gray-black.

It makes compounds with oxidation numbers of +2 and +4, but a +2 oxidation number is more stable. Oxides include yellow lead(II) oxide (PbO), red trilead tetroxide (Pb₃O₄), and black-brown lead(IV) oxide (PbO₂), which have been used as pigments since ancient times [8]. PbO has red tetragonal (α-type), yellow orthorhombic (β-type), and monoclinic crystals. Pb(NO₃)₂ is a white or transparent solid [5].

Radioactive materials such as uranium and thorium undergo repeated decay to produce lead, which is the final stable isotope.


## 2.2 Applications of Lead

Lead has long been used in a variety of applications. It has been used in batteries (storage batteries), lead electrodes (anodes) for the production of electrolytic copper foil, water pipes, coins, roofing materials such as roof tiles, solar panels, radiation absorber, sound insulation, seismic isolation equipment, and raw materials for soldering, and other things [7]. Solder is an alloy of lead and tin, and is a mainstream connection material for electronic components. Figure 1 shows a schematic diagram of the production of electrolytic copper foil, in which copper is used as an electrode (anode) in the production of electrolytic copper foil used in printed circuit boards such as personal computers.

![Figure 1 Schematic Diagram of the Production of Electrolytic Copper Foil](image)

Lead compounds also have a variety of applications. PbO, for example, is added to glass to increase its refractive index, and those with a content of 24% or more are called crystal glass. It is also used as a raw material for fluorescent lamps and stabilizers for vinylchloride resin [7]. Major application for PbO is the electrodes of batteries. Other uses are as a hardener in the manufacture of plastics used in sash putty and architectural sealants. The main uses of Pb(NO\textsubscript{3})\textsubscript{2} are raw materials of matches and explosives [8].

In recent years, due to its accumulative nature to living organisms, its effects on wildlife and soil contamination have become an issue, and alternative materials have been developed. The demand for lead is currently declining, with consumption of around 200,000-300,000 tons per year.

## 2.3 History of Lead

The history of lead and mankind is ancient and can be traced back to the Neolithic period in 6400 BC. Due to its ductility and softness, lead was used for various applications, including water pipes in the Roman Empire. It can be fused with copper (Cu) and antimony (Sb) to adjust its properties. Therefore, lead played an important role in the evolution of industry. Lead was produced in large quantities until the 20th century and was widely used in gasoline, paints, lead batteries, radiation absorbers and as a stabilizer for polyvinyl resins. However, accumulation of lead in the human body causes neurotoxic effects with various symptoms. The toxicity of lead and the symptoms of lead poisoning have been known since ancient times; there are records of high incidences of lead poisoning
and high mortality rates among those who were engaged in the smelting and processing of lead in the mid-19th century. The main reason for this is the accumulation of floating lead dust and lead compounds in the body from the mouth and nose. However, it was not until the mid-20th century that actual measures were taken [9]. For example, Japan now has a standard of 0.01 mg/L or less of lead for both water and soil pollution. The use of lead in gasoline and paint is now banned in Japan [7].

3. METALS OTHER THAN LEAD

Dangers of contamination by metals other than lead in fires and a case study of a past fire are presented in the following sections.

3.1 Metals Other than Lead Used as Building Materials [10]

Metal materials commonly used as building materials can be broadly divided into two categories: steel materials and nonferrous metals such as aluminum and copper.

The main metals that are fire hazards among metal materials are aluminum (Al), iron (Fe), titanium (Ti), magnesium (Mg), and nickel (Ni), which become hazardous under the following conditions [11-13].

1. Metal fires such as Fe, Ti, etc. in oxygen and chlorine piping systems
2. Fire of cutting oil in metal processing, organic abrasives cutting and abrasive debris
3. Fires caused by abnormal heat generation between Al and halogenated solvents or grease

Metals can produce irritating, corrosive, and toxic fumes in the event of a fire and can be harmful to the environment in general, but Ni in particular is second only to lead as an environmental hazard. Ni releases irritating and toxic fumes and gases in the event of a fire. Inhalation of fumes can cause pneumonia: they rarely evaporate at 20°C, but when diffused, the particles can rapidly reach toxic concentrations. When burned, it also produces toxic gases and vapors (nickel(II) oxide) and carbonyl nickel. It is also harmful to aquatic life and can have long-term effects [14, 15].

3.2 Examples of Environmental Pollution from Fires Caused by Metals Other than Lead

1. Pollution of rivers due to warehouse fires [16]

In 1986, a fire at a warehouse of the Sandoz’s agrochemical plant in Basel, Switzerland contaminated the Rhine River with chemicals, causing an acidic fog to engulf the city of Basel, staining the Rhine River red with runoff. It also caused diffusion of mercaptans, sulphur dioxide, nitric oxide, and ammonia because of smoke from the fire. To extinguish the fire, approximately 10,000 m³ of water was used to put out the fire and Rhine River was contaminated by disulfoton, an organophosphorus pesticide and mercury-based
fungicide that reached the river. The contamination reached the North Sea via the Rhine through France, then West Germany and the Netherlands, killing fish and livestock in the basin and imposing water intake restrictions.

(2) Soil contamination due to a fire in a hazardous materials warehouse [17]

A 2015 fire at a hazardous materials warehouse in Tianjin, China, caused multiple explosions due to poor handling of nitrocellulose, which led to a fire; the fire spilled several chemicals, including sodium hydroxide, sodium cyanide, ammonium nitrate, potassium nitrate, metallic magnesium, and sodium sulfide; soil and water sources were contaminated with cyanide, and sulfur dioxide, hydrogen cyanide, hydrogen sulfide, and ammonia were spilled into the air.

(3) Oil field fires caused by the Gulf War [18-20]

The 1990 Gulf War, which broke out as a result of the Iraqi invasion of Kuwait, set a number of oil wells ablaze, spewing crude oil from the wells and contaminating the surrounding deserts and spilling oil into the Persian Gulf. The oil spill killed the vegetation in the deserts and rendered the Persian Gulf inanimate, and contaminated the atmosphere with soot, sulfur dioxide and nitrogen dioxide, with consequences for the entire planet.

(4) Chlorine gas generated by a warehouse fire on a military base [21, 22]

A fire at a hazardous materials facility on the U.S. Kadena Air Base in Okinawa, Japan, in 2020 resulted in a chlorine gas spill; the facility primarily stores calcium hypochlorite, and the water used to extinguish the fire has not leaked outside the base, according to their report.

(5) Toxic substance spill resulting from an explosion and fire at a petrochemical plant [23, 24]

In 2005, an explosion and fire at a petrochemical plant in Jilin City, Jilin Province, China, spilled nitrobenzene into the Songhua River and polluted the river; the contaminants flowed up the Amur River and into the Sea of Okhotsk; this led to water intake restrictions in the basin and the detection of nitrobenzene and its metabolite, nitrophenol, in the fish.

(6) Large-scale oil tank fire [25]

In 2009, a fire at an oil refinery in the U.S. territory of Puerto Rico set 17 oil tanks ablaze; the fire was caused by gasoline overflowing from one tank, which spilled large quantities of oil into rivers and the ocean, and the fire also produced black smoke containing toxic substances.

(7) Contamination of soil by forest fires [26-28]

The 2007 forest fires in northern California, USA, which spread over a vast area and into residential areas, are believed to have contained heavy metals, polycyclic aromatic hydrocarbons, dioxins, and other toxic substances in the ashes, and there are concerns
about contamination of soil and rivers. The April 2020 fires at Chernobyl, Ukraine have raised not only similar concerns as California’s but also the spread of radioactive materials from the fallout residue from the nuclear power plant accident. Study finds 30 times more radioactive material at the site of the fire than the surrounding area.

(8) Fire caused by the Great East Japan Earthquake [29, 30]

Fires at oil-related facilities in Kesennuma City, Miyagi Prefecture, and Yamada Town, Iwate Prefecture, following the 2011 Great East Japan Earthquake and subsequent tsunami contaminated oil spills, which led to the detection of polycyclic aromatic hydrocarbons and other organic carbon compounds in shellfish collected from the surrounding waters (along the Sanriku coast) and sediments on the seafloor.

(9) Air pollution from peat fires [31-33]

In recent years, fires in peatland in Indonesia have caused serious air pollution due to particulate matters, so-called PM2.5, and carbon monoxide, etc. With economic development and population growth in Indonesia, forest fires and peatland fires due to slash-and-burn have been frequent due to increased demand for agricultural land.

(10) Asbestos spreading due to forest fires [34]

A forest fire in southeast Australia in 2018 spread into a residential area, and asbestos was scattered around the area and access was restricted.

4. LEAD AND FIRE IN BUILDING MATERIALS

In the previous section, the fire and environmental effects of metal materials other than lead were described. In this section, the use of lead as a building material and its effects on fire are discussed. First, the Kanazawa Castle, which has historically had many fires, is discussed, followed by a recent example of a fire involving lead paint on the Nakayoshida Expressway and the role of radiation protection in fire.

4.1 Lead Tiles of Kanazawa Castle

Kanazawa is a historic castle town, and even today the silvery lead tiles on the roofs of the Ishikawa Gate and the Sanjikken Nagaya can be seen in Kanazawa Castle (Figure 2). It is said that the roof tiles of Kanazawa Castle were first replaced with lead tiles in 1665, during the reign of Tsunanori Maeda (1645-1723), the fifth lord of the castle. The reason for the switch to lead tiles is that Japan’s feudal government at the time prohibited the use of coinage by each domain, and so large amounts of lead stored for gold and silver refining were reused. There are many theories about the purpose of the switch to lead tiles, such as that it was designed to be used as a fireball in an emergency, or as a countermeasure against snow, or that it was converted to a castle to show off the lead that would be turning to oxidized silver over time [35].
Kazuhiro Ozawa and Mamiko Horiki analyzed lead tiles of Kanazawa Castle from a private collection and found that the purity of the lead exceeded 97% and that almost 100% of the lead was used in the tiles without any mixture [35]. These lead tiles were decorated with the plum flower pattern, the family crest of the Maeda family of the Kaga domain. The upper half of the roofing tile's upper eaves shows stripes that were melted in the fire, and the lower half of the tile is thought to have turned black from the immediate area of the tile to the sides, and to have been smoked and turned black by the smoke of the fire. Figure 3 shows a measured drawing of the analyzed lead tiles.

As can be seen on the above-mentioned lead tiles, Kanazawa Castle was prone to fires, with 56 fires occurring between 1602 and 1859. This was caused by the fane phenomenon in early spring and early summer, lightning strikes in winter, and mismanagement of
Fires. Even after the Meiji era, a fire broke out in 1881 due to the accidental fire by army infantry stationed in the army barracks at Kanazawa Castle, destroying all the buildings in the castle except the Ishikawa Gate and the Sanjikken Nagaya. It is said that the lead tiles melted like a waterfall during the fire and it was not possible to remove the items inside the buildings.

4.2 Fire Involving Lead Paint on the Nakayoshida Expressway

In the fire that occurred under the Nakayoshida Viaduct on the Tomei Expressway on November 21, 2019, one worker who was repainting the bridge at the time died and 10 others were transported to the emergency room [36]. Based on the report of the Committee to Prevent the Recurrence of Fires Caused by Repainting of the Nakayoshida Viaduct on the Tomei Expressway, the cause of the fire was investigated and recurrence prevention measures are described below [37].

Paint used up to around 1990 contained lead dye to prevent rust, and around 2013, there were a number of cases of lead poisoning among workers who were repainting the paint across Japan. One possible cause is that workers inhaled lead-containing paint that had flown into the air when repainting a bridge. At the site where the lead-poisoned workers were found, the paint was applied around 1990. There are still many sites across Japan where such paint was used, so moisture was needed at the site to prevent dust from being spread during the repainting process. Figure 4 shows basic process of paint manufacturing. There are lead compounds that serve as paints and contain a flammable component.

![Figure 4 Basic Process of Paint Manufacturing [38].](image-url)
In the repainting process, the original paint is removed and a new coat of paint is applied, but the existing coating on the bridge girders contained toxic substances such as lead. Therefore, at the Nakayoshida Expressway site, moisture was maintained under the wet process and curing sheets were placed underfoot to prevent the stripped paint from becoming powdery and flying into the air. A ventilation system was installed to prevent workers from being poisoned by the alcohol contained in the stripping agent, but it was not operated because natural ventilation was maintained to a certain degree on that day. The fire occurred during the paint stripping process, and the possible ignition materials included cutting and shorting of electrical wiring and equipment, and sparks from electrical tools. Possible combustibles were curing sheets and paint chips.

Combustible materials that were thought to be the cause of the fire spread were investigated, and the curing sheet alone burned and melted temporarily when ignited, but no fire spread was confirmed. However, the fire spread when the scrap paint ignited, and the combustion temperature increased as the number of days left after the scrap paint peeled off increased. Aqueous-based paint strippers are not flammable in liquid form but contain 30-50% alcohol in their components. It was confirmed that the paint scraps containing the stripper emit alcohol-based vaporization substances that could be flammable depending on the concentration and other conditions, and the specific gravity of the vaporized substances emitted was higher than that of air.

The Fire Accident Recurrence Prevention Committee decided to prohibit tools that emit sparks from being brought into the scaffolding during the paint removal work, and to use electrical equipment with explosion-proof performance. All sheets, including curing sheets, were to be fire-retardant or flameproof. Scraped-off paint scraps were collected promptly and carried out of the scaffold at least once a day. It was also decided that the ventilation equipment was to be placed at a low position at each paint film peeling point and used constantly, and gas detectors to take measurements at a lower location where flammable gases are more likely to stay.

### 4.3 Radiation Protection in Fires

The next section considers the appropriate response to a fire in a facility that uses radioactive isotopes. For self-protective initial firefighting, ABC powder fire extinguishers should be used to reduce the possibility of radioactive contamination. Water discharge may be required for unsealed radioactive isotopes depending on the severity of the fire, and efforts should be made to quickly move the radionuclides with severe concentration limits. If there is enough time for evacuation, it is desirable to store them in a storage facility. Although the sealed radioisotopes can be stored in containers unless the fire is very severe, depending on the severity of the fire, there is a possibility that the containers may be damaged due to thermal damage, and the spread of contamination can be prevented to some extent by building a barricade with sand bags provided at the facility.

The initial firefighting is the keystone of firefighting activities in facilities that use radioisotopes. The arrival of the firefighting team may be delayed in case of earthquake-
induced fires, and the firefighting team should be prepared to put out the fires in the initial stages. The following is a description of the two types of initial firefighting measures for radioisotopes in the unsealed condition and the measures for the case where the fire is sealed by lead or containers (made of plastic, metal, or ceramic materials) [39].

First of all, when extinguishing the fire in the presence of unsealed radioactive materials, since the containers may be damaged, it is better to use ABC powder extinguishers (filled with powdered chemical agents (the main ingredient is ammonium monophosphate), which can extinguish over a wide range of fire [40]. Nuclides with strict concentration limits, such as $^{32}$P and $^{125}$I, should be moved out of the area immediately with an eye to extinguishing the fire with water discharge. If the fire is judged to be of a size that requires water discharge, it is necessary to deal with the fire by spraying water to prevent damage to the container. It is considered appropriate to return unsealed radioactive isotopes to the storage room when there is room in the initial firefighting phase. This is because the storage room is a robust fireproof structure with fire dampers to block ventilation [41].

Taking them out of the controlled area as an evacuation is not desirable because of the risk of loss. If there is an emergency, one option is to store it in a hood in the laboratory. In the hood, the possibility of contamination and dispersal during firefighting can be reduced. It should be noted that the air may be contaminated, so it may cause internal exposure to the workers through inhalation of the contaminated air.

Secondly, in the case of sealed radioisotopes, which are generally covered with lead and encapsulated in heat-resistant capsules, there is little possibility of contamination by the source itself. However, thermal damage can cause the shielding material to melt and the leakage rate of a highly radioactive sealed source can increase rapidly. In such cases, the emergency measure is to barricade the source with sand bags that are placed in each laboratory. The reason is that the main ingredient of the sand is silicon oxide, which has a relatively high effective atomic number and is considered to have a certain shielding effect.

Even in buildings that require radiation protection, lead-free building materials are increasingly used. However, the priority for the firefighting is not the prevention of scattering of lead but the radiation control.

5. LEAD AND FIRE IN ENERGY MATERIALS

Lead and fire in energy materials are discussed in the following sections.

5.1 Lead Toxicity and Detoxification of Leaded Gasoline Pollution

The problem with lead is due to its toxicity. When lead ions enter the human body, they bind to proteins and replace the metal ions that are supposed to be there, interfering with biological functions [42].
5.1.1 Lead Toxicity

An example of a protein that is poisoned by lead ions is 5-aminolev phosphate dehydrogenase, which is involved in heme synthesis. This enzyme performs the first step in the formation of the heme ring and uses zinc ions to catalyze the reaction. The lead ion is replaced by the zinc ion and the enzyme is deactivated. This prevents it from making new heme groups and causes anemia, one of the symptoms of lead poisoning [42, 43].

In addition to this, lead can cause symptoms of poisoning. This is because lead builds up slowly in the body. It disappears from blood proteins in about a month, but it can accumulate in the brain for years and in bones for decades. Proteins involved in the development of the nervous system are highly sensitive to lead, so they are particularly dangerous to developing children.

Due to the toxicity of lead, efforts are now being made to reduce the opportunities for lead exposure. In the following section, accidents caused by leaded gasoline and efforts to detoxify the environment are specifically discussed.

5.1.2 Accidents Involving Leaded Gasoline

On December 9, 1974, two Japanese employees who were cleaning fuel tanks at the Atsugi Air Base contracted tetraethyl lead poisoning, of which one died 18 days later and the other was discharged after two months in the hospital. The latter’s symptoms disappeared after six months of exposure, but the lead in blood and urine levels remained high.

The tank where the accident occurred had an oil leak on September 30 of the same year and the gasoline inside was transferred to the Tsurumi refueling plant. Subsequently, manholes at the top and bottom of the tank were opened to allow for better ventilation inside the tank, and the tank was left unattended for one to two months. Prior to the cleanup work, the tank was measured several times with a combustible gas detector, but no gasoline was detected in the tank. However, after the work was completed, both workers complained of nausea and vomiting for a time. The fuel stored in this tank were found to contain 1.12 mg/ml of tetraethyl lead (as lead) and to be aircraft leaded gasoline [44].

5.1.3 Efforts to Abolish Leaded Gasoline

Due to the impact of leaded gasoline on the environment and human health, efforts are being made around the world to make leaded gasoline pollution harmless. According to the National Petroleum Association, the number of gas stations across Japan decreased from 56,444 to 34,706 between 1998 and 2013, resulting in abandoned gas station sites. Leaded gasoline with alkyl lead was sold at these gas stations until 1986, and the soil at former gas station sites has also been subject to lead contamination due to leaks during refueling. In the U.S., according to the U.S. Environmental Protection Agency, leaded gasoline had been sold since the 1920s, but as a result of restrictions on the addition of alkyl lead to gasoline, lead levels in gasoline plummeted from 0.53 g/L in 1973 to 0.03 g/L in 1986 [45].
In Japan, in May 1970, a private organization conducted medical examinations of residents in Ushigome-Yanagi-cho, Shinjuku-ku, Tokyo, Japan and diagnosed a number of residents with lead poisoning as a result. This incident led to concerns about the effects of lead in automobile exhaust on the human health, and in July of the same year an administrative guidance was issued to limit the amount of lead added to automobile gasoline to 1.1 ml/gal or less. Then in August of the same year, a plan to implement unleaded gasoline for cars from April 1974 was announced, and the oil industry prepared for this change through administrative guidance. Since no leaded gasoline is currently sold, Japan is classified by the United Nations Environmental Programme as a country with a maximum lead concentration of 0.00-0.15 g/L in gasoline, with an average of 0.00-0.09 g/L [46].

5.2 Fire in Lead-Acid Battery

5.2.1 About Lead-Acid Battery

The lead-acid battery consists of Pb | H₂SO₄ | PbO₂, with anodes (negative electrodes) of Pb powder paste and Pb (0.1%) grids and cathodes (positive electrodes) of PbO₂ powder (paste) [47]. The cathode consists of a number of cathode plates connected in series or in parallel and then connected in series. The reaction formula for charging and discharging is as follows.

**Cathode:** PbO₂ + 3H⁺ + HSO₄⁻ + 2e⁻ → PbSO₄ + H₂O \[ E^\circ = +1.63 \text{ V vs. SHE} \]

**Anodes:** Pb + HSO₄⁻ → PbSO₄ + H⁺ + 2e⁻ \[ E^\circ = -0.30 \text{ V vs. SHE} \]

A control-valve stationary lead-acid battery is equipped with a negative electrode absorption reaction function, and under normal operating conditions, the electrolyte does not decrease, and rehydration is not required. The anode absorbs the oxygen gas generated from the cathode plate during charging, and the oxygen gas (O₂) generated from the cathode at the end of charging reacts with the spongy lead (Pb) of the anode active material to produce lead sulfate (PbSO₄) and water (H₂O). The reaction formula is as follows.

\[ 2\text{Pb} + \text{O}_2 + 2\text{SO}_4^{2-} + 4\text{H}^+ \rightarrow 2\text{PbSO}_4 + 2\text{H}_2\text{O} \]

In other words, the water lost by the generation of O₂ at the cathode is regenerated. In addition, the generation of PbSO₄ causes the anode plate to become discharged, so the amount of hydrogen gas generated from the anode is less than that of a liquid battery because the electrical energy of charging is used to reduce the PbSO₄ [48]. Due to the above functions, maintenance can be simplified because equal charging and measurement of the specific gravity of the electrolyte are not required. However, since the amount of electrolyte is reduced, it is easily affected by the ambient temperature.
5.2.2 A Case Study of a Lead Acid Battery Fire

According to the first meeting of the technical review group for storage battery systems of the Fire and Disaster Management Agency of the Ministry of Internal Affairs and Communications, there were a total of 688 fires reported to the Agency from 2010 to 2014 in which the ignition source was a storage battery. Of these, 19 fires were inferred to have been caused by lead-acid batteries, which accounted for about 2.8% of the total number of fires. In addition, 13 of the fires were thought to have been caused by inadequate maintenance, which accounted for 68% of the lead-acid battery fires [49].

The following is a case study of the fire that broke out in an emergency storage battery system [50]. The fire broke out in the electrical room on the second basement floor of the 17-story, fire-resistant building with two basement floors. There were no casualties from this fire. When normal power was cut off to test the power outage, smoke rose from the battery equipment panel of the emergency lighting system. When the person in charge cut off the power supply to the battery equipment panel that was emitting the smoke, the smoke was stopped.

The storage battery facility at the source of the fire consisted of 54 control-valve stationary lead-acid batteries of 200 Ah and 500 Ah capacity, for a total of 108 units. The burned out control-valve stationary lead-acid batteries in the uppermost row, one each of 200 Ah and 500 Ah, were damaged.

At the time of the accident, there was still a plenty of time to the deadline for the replacement of the storage batteries, and the ambient temperature in use was listed as 25°C. The records of the monthly inspection of the storage batteries showed that the temperature in the room on the day of the fire was about 20°C, but the previous year’s records showed that the temperature was higher.

The fire was caused by poor contact between the anode strap and the anode plate due to corrosion caused by deterioration. When normal power supply was cut off for inspection and the power was supplied from lead-acid batteries for the emergency lighting system, sparks were generated at the contacting points between the anode strap and the anode plate, and the hydrogen stored in the system ignited and caused the fire. In the control-valve stationary lead-acid batteries, it is considered that the degradation of the anode plate caused the generation of more hydrogen than usual.

The lead-acid batteries for emergency lighting equipment that caused fire had been installed for 11 years. The manufacturer assumed a lifespan of 15 years when used in a room temperature of 25°C environment, but the lifespan may be shortened due to progressive deterioration in high temperature environments such as machine rooms. There is no law that regulates periodical inspection of control-valve stationary lead-acid batteries other than emergency power sources, and it seems that inspections were carried out about once every six months to a year as a voluntary standard. Degradation diagnosis was also carried out, but the building owner had to decide on the replacement of the batteries. Although the side panels of control-valve stationary lead-acid batteries clearly
state that the service life of the batteries decreases depending on the usage environment, especially the temperature at which they are used, the degradation is difficult to detect from the outside, and there is a high risk that degraded lead-acid batteries will continue to be installed as-is. Since control-valve stationary lead-acid batteries have a characteristic of halving the service life when the temperature rises by 10°C, there was a need for countermeasures in the industry.

Accordingly, the Battery Association of Japan has taken the following measures because there was a risk of ignition of the control-valve stationary lead-acid batteries used as an emergency power source.

(1) The manufacturers who were members of the Association were informed of the fire hazard of degraded control-valve stationary lead-acid batteries.

(2) The risk of fire was clearly stated in the pamphlet to raise awareness of the promotion of replacement of storage batteries that have reached the end of their useful life.

(3) In order to improve the degradation diagnosis of storage batteries, the technical guidelines for the degradation diagnosis of storage battery equipment issued by the Association were revised.

5.3 Lead Halide Perovskites in Semiconductor Materials in Solar Cells [51]

In recent years, there has been a flurry of researches into low-cost, lightweight and highly energy-efficient solar cell materials compared to silicon (Si) and gallium arsenide (GaAs) monocrystalline solar cells, one of which is lead halide perovskite (CH$_3$NH$_3$PbI$_3$).

CH$_3$NH$_3$PbI$_3$ thin films are aggregates of microcrystals ranging in size from a few tens of nanometers to microsizes, but they exhibit highly efficient band edge emission at room temperature. Although they are polycrystalline thin films composed of particles, they are semiconductor materials with few deep non-luminescent centers and trap orders. The bandgap conversion efficiency energy at room temperature is 1.61 eV, and the material exhibits high optical absorption derived from direct transition semiconductors.

The crystal structure of the lead halide perovskite semiconductor CH$_3$NH$_3$PbX$_3$ [X=Cl, Br, I] is shown in Figure 5, which is a three-dimensional perovskite structure consisting of PbX$_6$ octahedra with shared angles and CH$_3$NH$_3^+$ (MA$^+$) ions in the gaps. The exciton binding energy is estimated to be 30-50 meV at low temperature (~5 K).
However, the basic physical properties of the material are not fully understood at this time. Challenges to commercialization include material stability, device lifetime, and the inclusion of toxic lead. Since lead is toxic, development of lead-free perovskite solar cells is underway, but they are low efficiency and unstable. Recent researches have investigated mixing germanium with tin or materials containing tin and iodine [52, 53]. There have been no cases of fire accidents like in lead-acid batteries because they have not yet been commercialized.

6. CONCLUSIONS

One month after the fire at Notre Dame Cathedral, the city of Paris tested schools and kindergartens near the cathedral for lead levels and told the schools that there was no serious risk to their health. However, as mentioned at the beginning of the report, two nearby schools were closed in July of the same year due to the report of lead contamination by environmental groups and the media [3].

France resumed reconstruction work on Notre Dame Cathedral in late April, 2020, which had been halted because the city was on lockdown since mid-March 2020 due to the spread of the new coronavirus [54, 55]. The process of decontaminating the cathedral without damaging it is thought to take longer time than the usual decontamination process, and some people in France are calling for the reconstruction process to be carried out carefully.

Figure 6 shows a picture of the city of Paris in normal times and the fire extinguishing systems installed in the subway and shops. It is clear that the city of Paris is carrying out its fire prevention efforts. While it is common for people to wish things to return to normal as soon as possible, it is also important to convey the right information from a scientific perspective and take appropriate action when issues such as lead contamination remain.
This literature review shows that the human and environmental effects of lead from fires are still a problem not only in European buildings, but also in many parts of the world, including Japan, where lead regulations have become more stringent. The experience of Notre Dame Cathedral will leave us with lessons to be learned in the future when dealing with fire and lead decontamination in other buildings.

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