CONTAMINATION OF EXTINGUISHING WATER AFTER FIRES OF LI-ION BATTERIES

Work Package 1.4

ALBERO Project

Institut für Sicherheitstechnik/Schiffssicherheit e.V.

Contamination of extinguishing water after fires of Li-Ion Batteries

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Although there very many publications [1], [2] and instructions for fire departments and emergency services are available [3], [4], in which reference is made to the "contamination of the extinguishing water" when fighting a fire coming from electric vehicles, there have been surprisingly few thorough scientific studies on this subject until today.

In 2013, the National Fire Protection Association [5] published the results of extensive real fire tests. Complete Li-ion batteries from vehicles were used without describing their cell chemistry in more detail. However, the published analyses suggest that the cells were lithium nickel manganese cobalt oxide cathode (NMC) cells. The extinguishing water from two independent tests was chemically analyzed. Significant amounts of chloride and fluoride ions were found in each case, which was attributed to leaching of HCl and HF, respectively, from the fire gases. In both tests, the extinguishing water was slightly more acidic (pH = 6.2 and 7.3, respectively) than before the extinguishing operation (the extinguishing water used had a pH of 7.8).

Egelhaaf et. al [6] also found significantly increased concentrations of chloride and fluoride ions in samples of extinguishing water. These concentrations increased when the damaged battery was stored in cooling water overnight.

DNV-GL describes investigations with NMC and lithium iron phosphate (LFP) cells [7]. The thermal runaway was caused by overheating. During the bursting, HCl and HF gases were also measured in significant concentrations. The following statement was made about the extinguishing or cooling water: *Most notably, when submerged or extinguished batteries can produce a severely alkaline solution in the water used, climbing to pH 10-11. Other solutions gradually became slightly acidic (pH 6), where the most severely burned batteries produce the most basic solution.*

In [8], extensive real fire tests were carried out with NMC batteries. The thermal runaway was caused by mechanical damage. On the one hand, the extinguishing water which was collected directly during the fire-fighting process was investigated and, on the other hand, the cooling water was investigated which was used later to immerse the extinguished battery for safety reasons.

The following results were found:

Extinguishing Water
- pH value 8
- moderate electrical conductivity of just under 500 µS/cm
- low contents of water-soluble sulfates (34 mg/l), fluorides (8 mg/l), chlorides and nitrates (2 mg/l each), and lithium ions (4 mg/l)
- dissolved organic fire residues (PAH, PCB, PCDD/F) in very low concentrations
- Co, Ni and Mn in very high acid-soluble concentrations of 36 mg/l each

Cooling Water
- pH value 12
- very high electrical conductivity of about 35,000 µS/cm
- low levels of water-soluble sulfates (98 mg/l), chlorides (2 mg/l) and nitrates (<1 mg/l)
- very high concentrations of water-soluble fluorides (330 mg/l)
- very high concentrations of lithium ions (1,600 mg/l)
- organic substances resulting from fire (PAH, PCB, PCDD/F) only in very low concentrations
- Co, Ni and Mn in very high acid-soluble concentrations of 50 to 55 mg/l each

Summary and Conclusions

Despite the few data the following statements emerge relatively clearly:

- Extinguishing water that only comes into contact with the gases escaping from a lithium-ion battery dissolves parts of the acid gases that are produced (HCl, HF, HCN). The lapsing solution contains chloride and fluoride ions accordingly and reacts slightly acidic. The significance of this effect depends on the very specific cell chemistry (conducting salt e.g. $LiPF_6$ or $LiClO_4$), on the state of charge of the battery (affects the amount of escaping gases) and on the water extinguishing system used. In general, water mist systems are thought to be better to supress fire gases than sprinklers. However, strongly acidic solutions are not to be expected.
- Extinguishing water that comes into contact with the "internal components" of a battery, i.e. also with metallic lithium, reacts with this (and possibly other metals) to form hydroxides which react very strongly alkaline. This can occur if the battery has already been destroyed during the accident to such an extent that water can penetrate into these areas (this difference must also be taken into account during tests, i.e. whether the Thermal Runaway was triggered by overheating, overcharging or mechanical destruction). Complete immersion of the battery in a water-filled container will soon result in direct contact with its interior. These solutions also contain correspondingly high concentrations of heavy metals.

Literature

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