PP127316

Safety Review of Bromine-Based Electrolytes for Energy Storage Applications

ICL Industrial Products

Report No.: 1, Rev. 1
Date: February 26, 2016

Project name: PP127316
Report title: Safety Review of Bromine-Based Electrolytes for Energy Storage Applications
Customer: ICL Industrial Products,
Address
Contact person: Sharona Atlas and David Murphy
Date of issue: February 26, 2016
Project No.: **PP127316**
Organization unit: OAPUS304
Report No.: 1, 1
Document No.: No

DNV USA, Inc.
5777 Frantz Rd
Dublin, OH 43017
Tel: +1-614-761-1214

Task and objective: Create/Propose a Safety Testing Plan. To review Con Edison's existing safety related materials and identify gaps by cross checking with relevant standards in the industry. Assess the risk and consequences of potential hazards that may occur to the TESS. Recommend the approach and relevant testing in order to fill the identified gaps.

Davion M. Hill

Prepared by:	Verified by:	Approved by:
[Davion Hill, Ph.D.] [Group Leader, Energy & Materials]	William Kovacs III, P.E. Senior Engineer – Oil & Gas Fatigue and Fracture	[Name] [title]

Rev. No.	Date	Reason for Issue	Prepared by	Verified by	Approved by

Table of contents

1 EXECUTIVE SUMMARY

ICL Industrial Products (Israel Chemicals, Ltd) is a chemical company producing fertilizers, metals, and other special purpose chemical products. In particular, ICL's mineral extraction processes from the Dead Sea allow it to export up to 35% of the world's bromine production. Other major products include potash, magnesium, and phosphate. Because of ICL's justified interest in bromine-based electrolytes, there is a significant need for ICL to support the emerging energy storage market around bromine-based electrochemistry and related technologies. ICL wishes to support its emerging customers with technical advice, electrolyte development, safety recommendations, and best practices for materials handling.

The above sections outline the hazards associated with pure bromine, and it has been stated that the general safety concern is liberation of bromine from these bromine-based electrolytes. There may be additional hazardous materials considerations that arise from the specific properties of the bromine-based electrolyte composition, and this should be examined on a case-by-case basis, depending on the electrolyte chemistry.

A summary of the most relevant risks are related to the consequences of spills, human exposure, and the potential for release or evolution of bromine gas. The hazards that may lead to these consequences are (with greatest risk at the top):

1. Spills (such as during transport or installation) leading to human contact
2. Cell stack leakage leading to a spill or human contact
3. Br_2 gas evolution due to hazardous temperature or chemical condition
4. External Fire leading to bromine gas evolution

These risks have been identified as a product of probability and consequence with an adjustment factor associated with barriers that prevent these hazards from occurring. The following report explains the methodology for identifying the risks, what is presently being done to mitigate them, and what the industry might consider to enhance mitigation methods.

2 APPROACH

DNV GL routinely uses FMEA in tandem with Bowtie analysis for risk assessment. Commonly cited FMEA standards include IEC 60812 and MIL-STD-1692A. In addition, DNV GL's RP-A203 contains specific guidance on FMEA. FMEA and/or Bowtie analysis can be complimented by fault tree analysis as described in IEC 61025. Additional FMEA complimentary processes include HAZOP (IEC 61882), HAZID (ISO 17776). For this program and the generalized scope to cover multiple battery technologies, FMEA and Bowtie analysis are used in tandem to assess general risk metrics. The approach is shown in Figure 1. For a description of how Bowtie models are constructed and read, it is best to refer to the section titled "Bowtie Model Primer: How to Read and Interpret Bowtie Models" on page 1 of the Appendix.

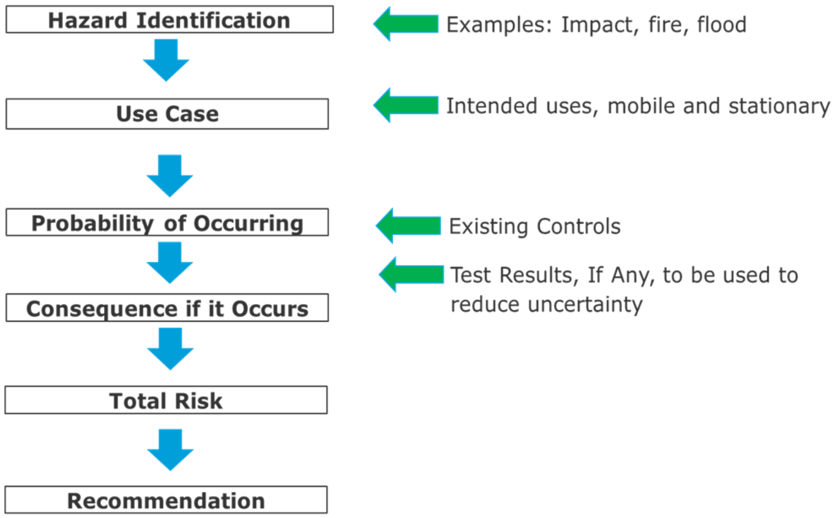


Figure 1 Identification of hazards and consequences during a risk assessment.

The general process for FMEA is to list all possible hazards and describe their link to consequences. Additional factors can be included such as barriers that prevent the hazards or consequence from occurring. The Bowtie model is like an event tree on the left side (hazard side) and a fault tree on the right side. The Bowtie, however, is not quantitative like a fault tree. It does illustrate pathways to failure, however. The Bowtie compliments the FMEA study because the number of barriers and their effectiveness are easily assessed and a qualitative ranking in the FMEA is facilitated. A barrier effectiveness rating can then be applied to the FMEA such that low probability, high consequence events can be "scaled" by the relative effectiveness of the barriers in place to prevent them. This iterative feedback process between the Bowtie and FMEA models is shown in Figure 2.

Finally, recommendations can be created from the FMEA + Bowtie analysis using the procedure shown in Figure 3. If testing is part of the solution, recommendations or investigations can be derived from the technical considerations of the equipment or procedure under scrutiny. Appropriate calculation or modeling tools can be employed to similarly solve problems related to barrier effectiveness or probability of failure modes. Such analyses are helpful for owner's engineer services, for example, where design features are tested or evaluated for efficacy, or independent engineer services where validity of claims or functions are required.

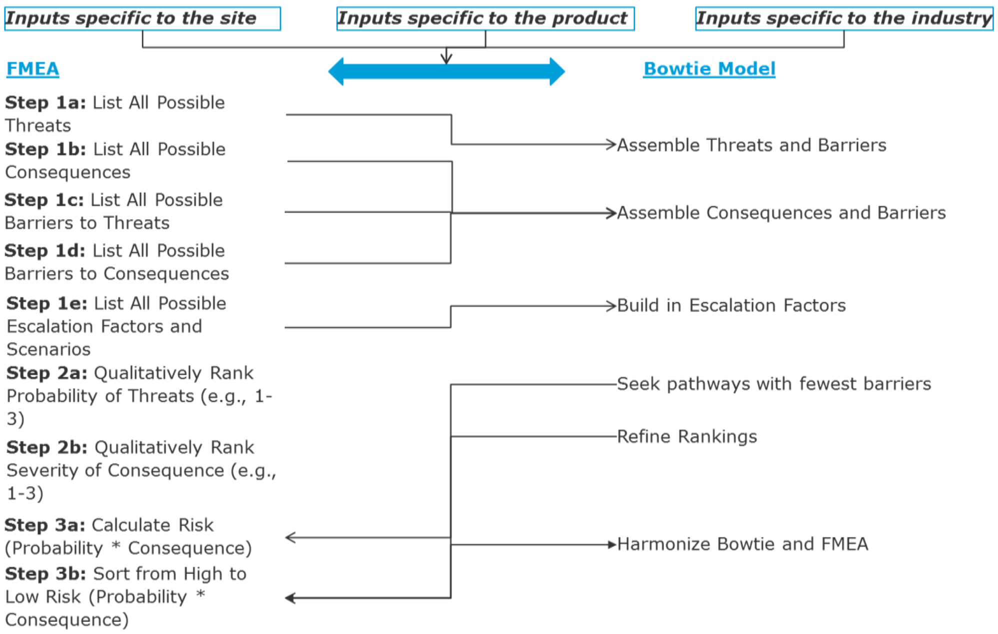


Figure 2 Parallel hazard assessment using FMEA and Bowtie models in tandem.

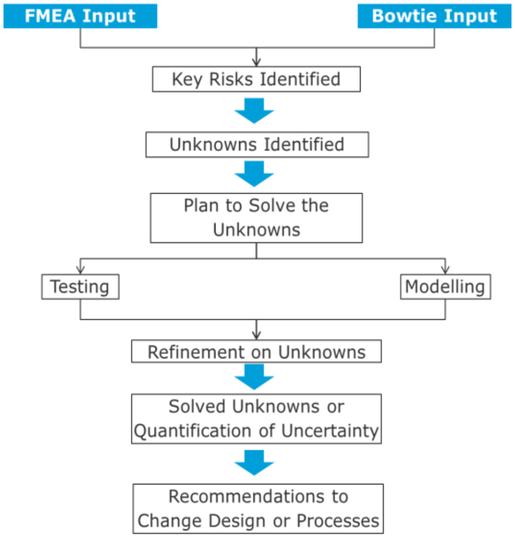


Figure 3 Creation of recommendations with Bowtie and FMEA models.

3 BOWTIE MODEL

As mentioned above, the left side of a Bowtie model is an event tree. The right side of a Bowtie model is a fault tree. While no probabilities are assigned to the pathways in the model, the Bowtie diagram is a mechanism to view threats, barriers, and pathways to consequences in a rapid manner.

In this program, DNV GL identified several incident pathways of interest[1] (see Appendix for details). These include:

1. Hazardous temperature condition or external fire elevating the temperature to > 50°C leading to bromine gas evolution from the electrolyte
2. Electrolyte spills due to impact or mishandling
3. Human health hazards associated with exposure from spill, stack corrosion and leakage, or other chemical phenomena

---

[1] See "Incident Pathways on page

4. DNV GL investigated mechanisms that may lead to a "hazardous chemical condition" which would involve inadvertent degradation of the complexing agent. No significant causes of this hazard were identified.

External fires are a hazard that exists[2] regardless of whether a battery system is equipped with an automated fire extinguisher. The hazards that must be considered are related to building occupants, first responders, and/or post-incident clean-up crews. Automated fire extinguishers are commonly installed in ESS in order to suppress or defeat incipient fires before they spread to critical components of the ESS. Such systems are more common for Li-ion systems or lead acid battery systems (such as UPS) because of the thermal runaway hazard for both, and potential for hydrogen evolution from lead acid systems.

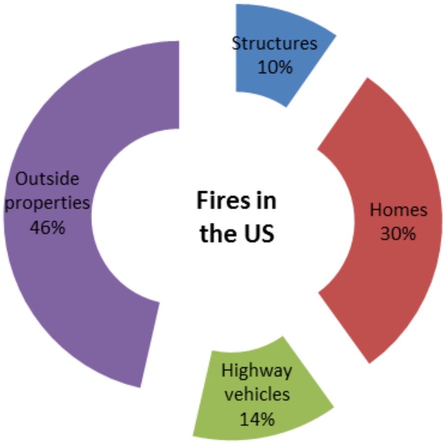


Figure 4 Fire statistics in the US.

Because the Zn-Br electrolyte is not considered flammable, automated fire suppression systems appear to be considered a minor need (and therefore the fire suppression barrier in Figure 6 does not exist) for the Zn-Br battery system. However, as shown in Figure 4, the threat is not necessarily an internal system fire, but an external fire. The NFPA states there are more than 1.2 million fires in the US annually of which 10% are in structures and 46% are outdoors and may be near buildings (Figure 4). The purpose of an automated extinguisher system on a Zn-Br battery, if equipped, would be to delay or prevent a fire from consuming the battery, heating the electrolyte tanks, and causing evolution of Br gas. An identified gap is the lack of protections to disrupt this incident path if it were to occur.

Temperatures reaching 50-60°C or higher in a Zn-Br flow battery system are highly unlikely without a fire. However, the location dependence of the storage will be a determining factor in the temperatures the system may experience, for example, if the storage device is in direct sunlight, or is installed in unconditioned spaces. Some systems do not have onboard HVAC for internal climate control, and hence the temperature control barrier does not exist for some systems which weakens the effectiveness of this barrier path.[3] There is concern that some systems can create internal heat that is greater than 35°C, and hence any elevation in ambient temperature can increase the probability of this hazard. In populated areas, the risk of third party damage is always a concern. Contractors using power equipment for demolition or excavation represent a significant hazard for many types of property. Handling of the system during transport or installation represents a higher risk period because of increased activity near the system. Because many of

---

[2] Karter, Michael. "Fire Loss in the United States During 2013". NFPA, September 2014.

[3] Please see Appendix, "Complexing Agents" and "Flammability and Evaporation Risk"

these ESS systems are intended for behind the meter (BTM) applications there is a need to assess the risks of that environment related to physical integrity. Forklifts other nearby traffic can threaten the integrity of the system unless appropriate barriers and safeguards are in place. Another hazard that may lead to spills or containment failure can be corrosion or leakage of the cell stack itself. This has been referenced as a prior hazard by one of the respondents to the program [see Battery Manufacturer Questionnaire in the Appendix]. Lastly, the stability of the complexing agents used for Zn-Br systems was also investigated. The main hazard to complexing agent integrity is temperature. Again, above 50°C the boiling point of bromine can be reached such that it can be liberated and evaporated from the Zn-Br electrolyte. Otherwise, no major contaminant hazards for the complexing agents were identified.

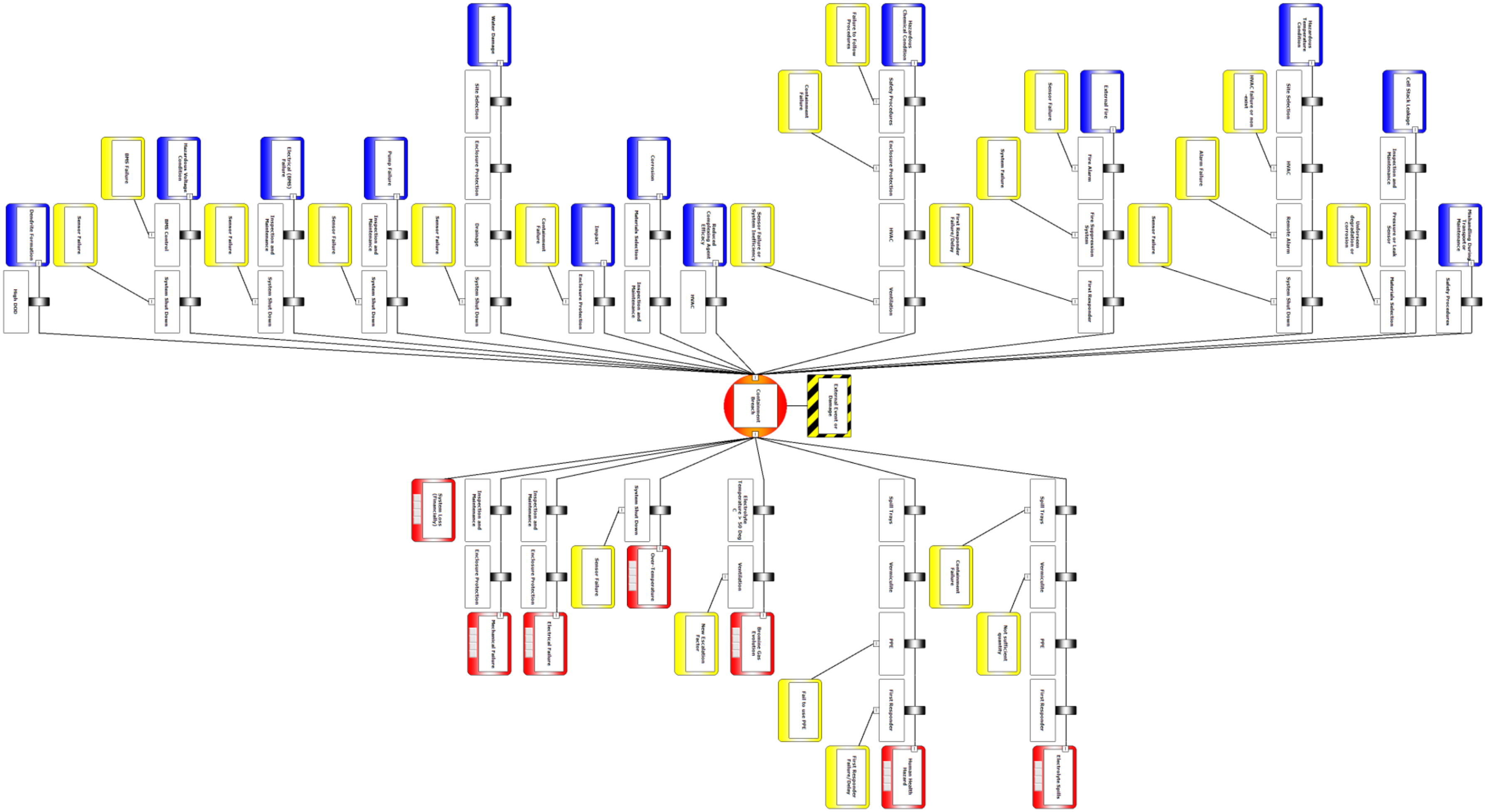


Figure 5 Bowtie model.

3.1 Incident Pathways

With the basis of the model constructed, incident pathways to key elements can be explored in more detail, the barriers can be directly identified, and the effectiveness of the barriers can be evaluated. Below are incident paths for incidents related to bromine gas evolution, electrolyte spills, and human exposure.

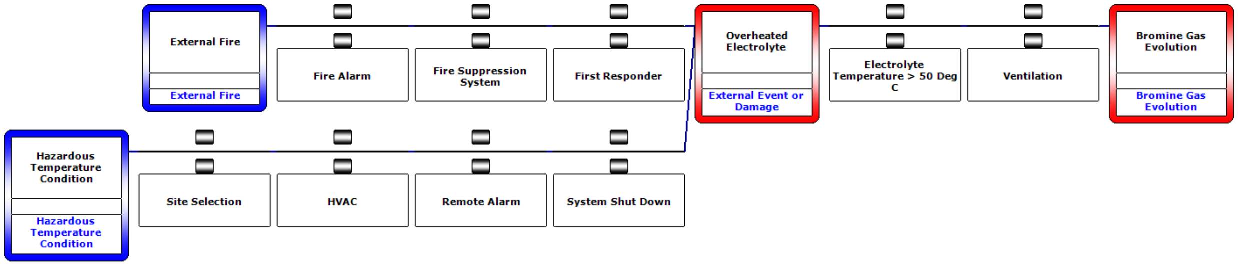


Figure 6 Fires or hazardous temperatures leading to bromine gas evolution.

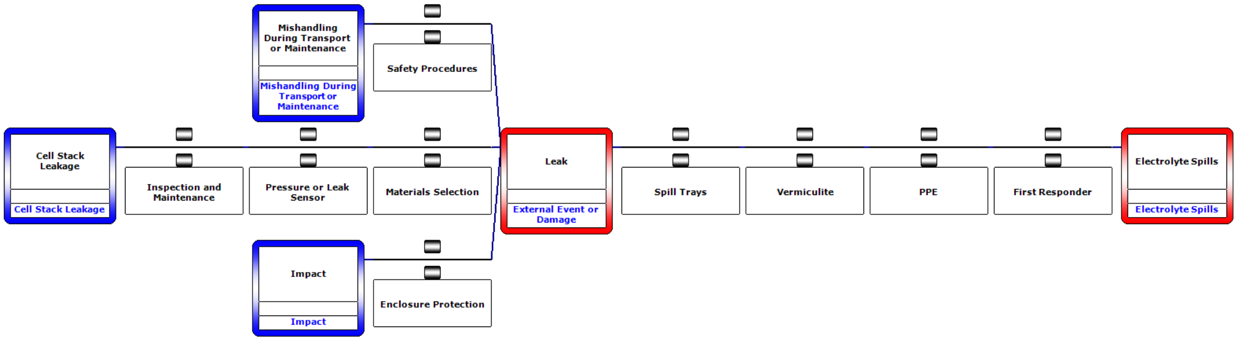


Figure 7 Mishandling, impact, or stack leakage leading to an electrolyte spill.

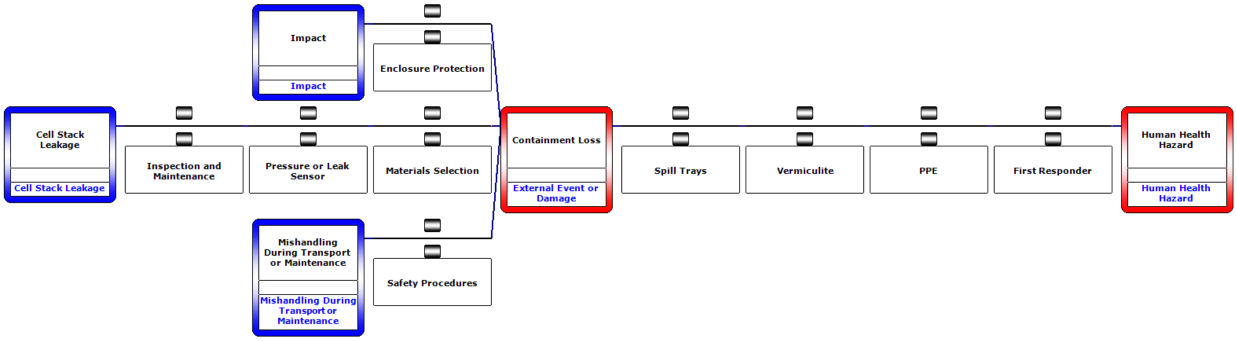


Figure 8 Incident path: cell stack leakage leading to electrolyte spill or human health hazard.

4 FMEA OUTPUTS

The failure mode effects analysis (FMEA) exercise generated the result shown in Table 1. In the table, each specific hazard is captured in a hazard category used in the bowtie model. The potential consequences are listed along with an aggregated risk score for each hazard. The aggregated risk score is represented as a stop light with risk levels: Red = High, Yellow = Medium, and Green = Low. High risk hazards are those with high probability of occurrence and high consequence. Low risk hazards are those with low probability of occurrence and low severity of consequence. The risks with the hazards were ranked by looking at the number of barriers preventing the hazard, effectiveness of the barriers and the severity of the consequence. While the incident pathways identified in the Bowtie model were qualitative, the FMEA presents a method to assess the relative risk of each. As identified in the FMEA, the top 4 risks are:

1. Spills (such as during transport or installation)
2. Cell stack leakage
3. Br evolution
4. External Fire

Table 1 Summary of FMEA findings.

Hazard or Top Event	Relevant Bowtie Hazard Category	Causes	Consequences	Scaled Risk
Electrolyte Spills During Transportation/Install	Hazardous Chemical Condition	Vehicular Accident, Mishandling	Human Health Hazard	🔴 6.0
Cell Stack Leakage	Cell Stack Leakage	Corrosion, Equipment Failure, Manufacturing/Design Defects	Human Health Hazard	🔴 4.5
Br Evolution	Hazardous Chemical Condition	Temperature >50-60 C	Human Health Hazard	🔴 4.5
External Fire	External Fire	Building Fire, Arson	Br Evolution, Human Health Hazard	🟡 4.0
Electrical System Failure	Electrical (BMS) Failure	Corrosion, Equipment Failure, Manufacturing/Design Defects	Over-Temperature, Br Evolution, Equipment Loss	🟡 4.0
Corrosion	Corrosion	Equipment Flooding, Condensation	Electrical Failure, Electrolyte Spill, Pump Failure	🟡 4.0
Forced Discharge	Hazardous Voltage Condition	Electrical Failure, Mishandling	Over-Temperature, Br Evolution	🟡 4.0
Reduced Complexing Agent Efficacy	Reduced Complexing Agent Efficacy	Temperature >60 C or <0C	Increase in Br vapor pressure	🟡 2.7
Over-Discharge	Hazardous Voltage Condition	Electrical Failure, Sensor Failure	Over-Temperature, Br Evolution	🟡 2.7
Electrolyte Spills During Operation	Hazardous Chemical Condition	Containment Failure	Br Evolution, Human Health Hazard	🟡 2.7
Over-Temperature	Hazardous Tempearture Condition	Ambient Temperature, External Fire	Fire, Br Evolution, Human Health Hazard	🟡 2.4
Pump Failure	Pump Failure	Electrical Failure, Corrosion, Mechanical Damage	Electrolyte Spill, Human Health Hazard	🟢 2.3
Interconnection Short/Spark	Hazardous Voltage Condition	Mishandling, Water, Equipment Failure	External Fire, Equipment Damage	🟢 2.0
Dendrite Formation	Dendrite Formation	Partial Cycling	Over-Temperature, Br Evolution	🟢 2.0
Internal Fire	N/A	Over-Temperature, External Fire, Electric Short/Spark	System Loss, Building Fire, Collateral Damage	🟢 2.0
Degradation Products in Electrolyte	N/A	0	Precipitates that harm battery function	🟢 2.0
Improper Material Selection	Hazardous Chemical Condition	Labelling/Shipping Error	Human Health Hazard	🟢 1.3
Over-Charge	Hazardous Voltage Condition	Electrical Failure, Sensor Failure	Over-Temperature, Br Evolution	🟢 1.3
High Rate Discharge	Hazardous Voltage Condition	Electrical Failure, Sensor Failure	Over-Temperature, Br Evolution	🟢 1.3
Short Circuit	Hazardous Voltage Condition	Electrical Failure	Over-Temperature, Br Evolution	🟢 1.3
System Flooding	Water Damage	Flood, Rain	Equiment Loss, Financial Loss	🟢 1.0
Containment Failure	Impact	Corrosion, Impact, Structural Failure	Equipment Loss, Electrolyte Spill, Br Evolution, Human Health Hazard	🟢 0.6

The ranking of risks is not only dependent on the probability and consequence of the risk occurring, but also on the relative effectiveness of barriers. Barrier effectiveness ratings are shown in Figure 9. The calculation of the barrier effectiveness rating is shown below, where a “scaled risk” is derived while accounting for the number of barriers and their relative effectiveness.

For the severity of the consequence S, the expected severity is then conditional on whether the case has been physically tested, experienced, or otherwise known. Known testing results, industry or company experience, or operational history can indirectly reduce severity via reduction of uncertainties, and therefore the severity rating is used as the means to capture this knowledge. This can be called the “known severity” K. There may be different methods for calculating K. For example,

If tested K = (S-1)*E, Else K =S

Alternatively,

If tested K = S/c, else K=S

where c is some reduction factor in risk, i.e., c=2 or 3. In this case, DNV GL has chosen the latter method where c =1 because no prior testing results are included in this study.

And finally,

Risk = K*(1-E)

For each of the identified hazard, the number of barriers, both active and passive, are represented in Figure 9. The number of barriers for each hazard is used to determine the likelihood of occurrence. The barriers were assessed through interviews with battery vendors and system integrators. As can be seen, the number of barriers for each hazard varies with up to 3.5 for those related to containment and <1 for Br gas evolution.

With barrier effectiveness calculated, it is now possible to juxtapose the number of barriers preventing a hazard and the relative strength of their defeating mechanisms by graphing these factors on perpendicular axes. This is shown in Figure 10. This visualization of the risks aids in explaining what factors are high risk and which ones are not. For example, there are few barriers to prevent issues that could cause degradation of the complexing agent, however there are few mitigating factors for these barriers (i.e., technical factors that could cause complexing agent degradation, besides temperature, have not been identified). Hence this hazard is in the lower left quadrant of the chart. By comparison, there are many barriers that mitigate or prevent containment failure, and some of them can be defeated. Thus containment failure is in the middle right side of the chart. Bromine gas evolution has few barriers preventing it and there are strong mitigating factors for these barriers, and therefore Br gas evolution is in the upper left quadrant of the chart. This region (upper left) is the highest risk region.

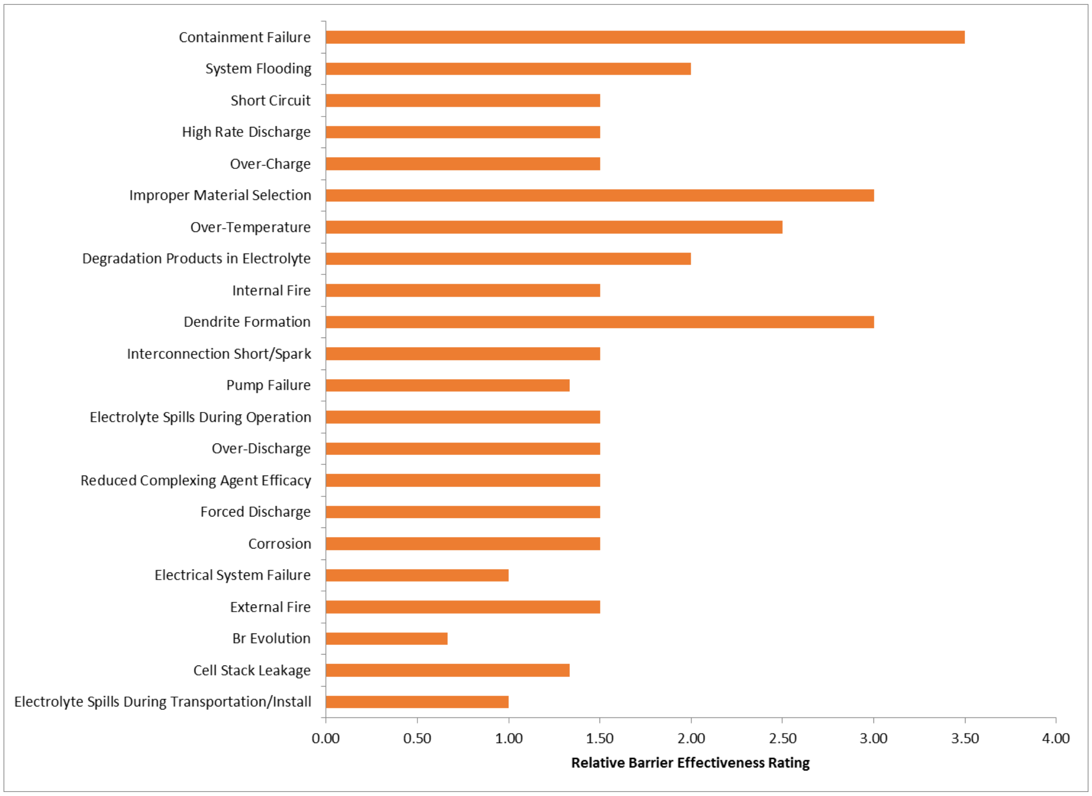


Figure 9 Barrier effectiveness

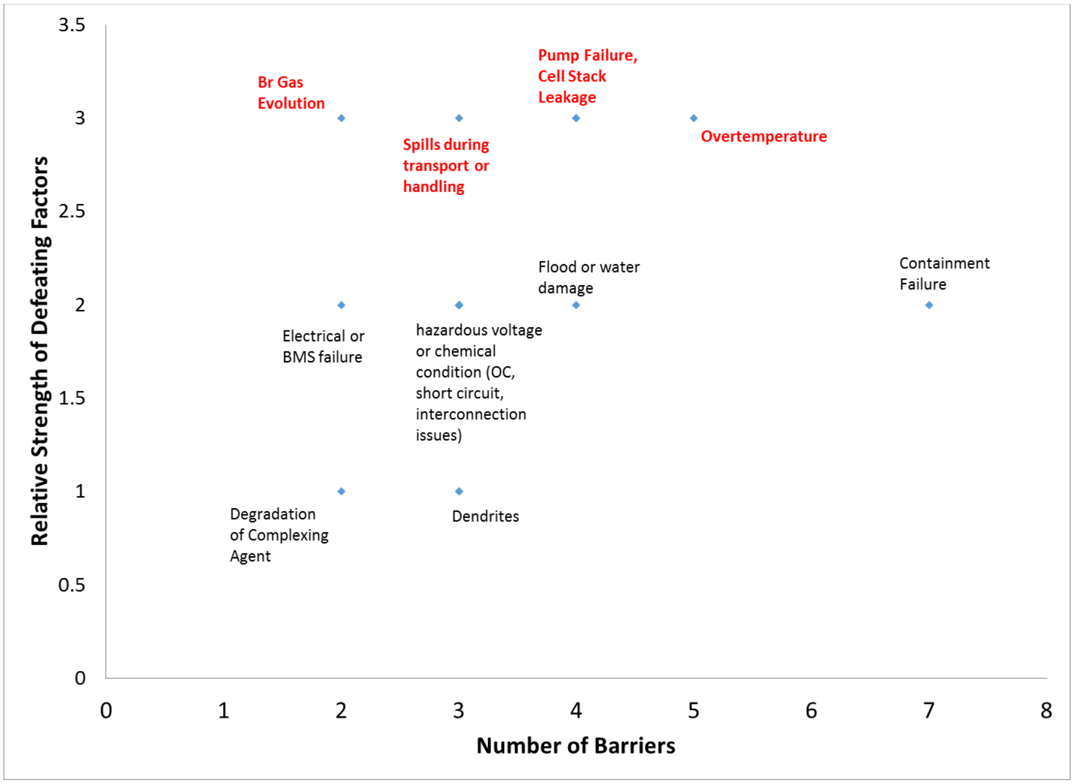


Figure 10 Barriers and defeating mechanisms.

Yet another way to visualize the risks is by plotting relative risk (qualitative probability * consequence) vs. scaled risk (which includes barrier effectiveness). This highlights simultaneously that some low probability events have significant defeating factors. When plotted this way (Figure 11) it can be seen that spills and Bromine gas evolution are in the upper regions of the risk chart, near the upper right section. Leakage and hazardous temperature conditions are similar hazards that are also ranked highly.

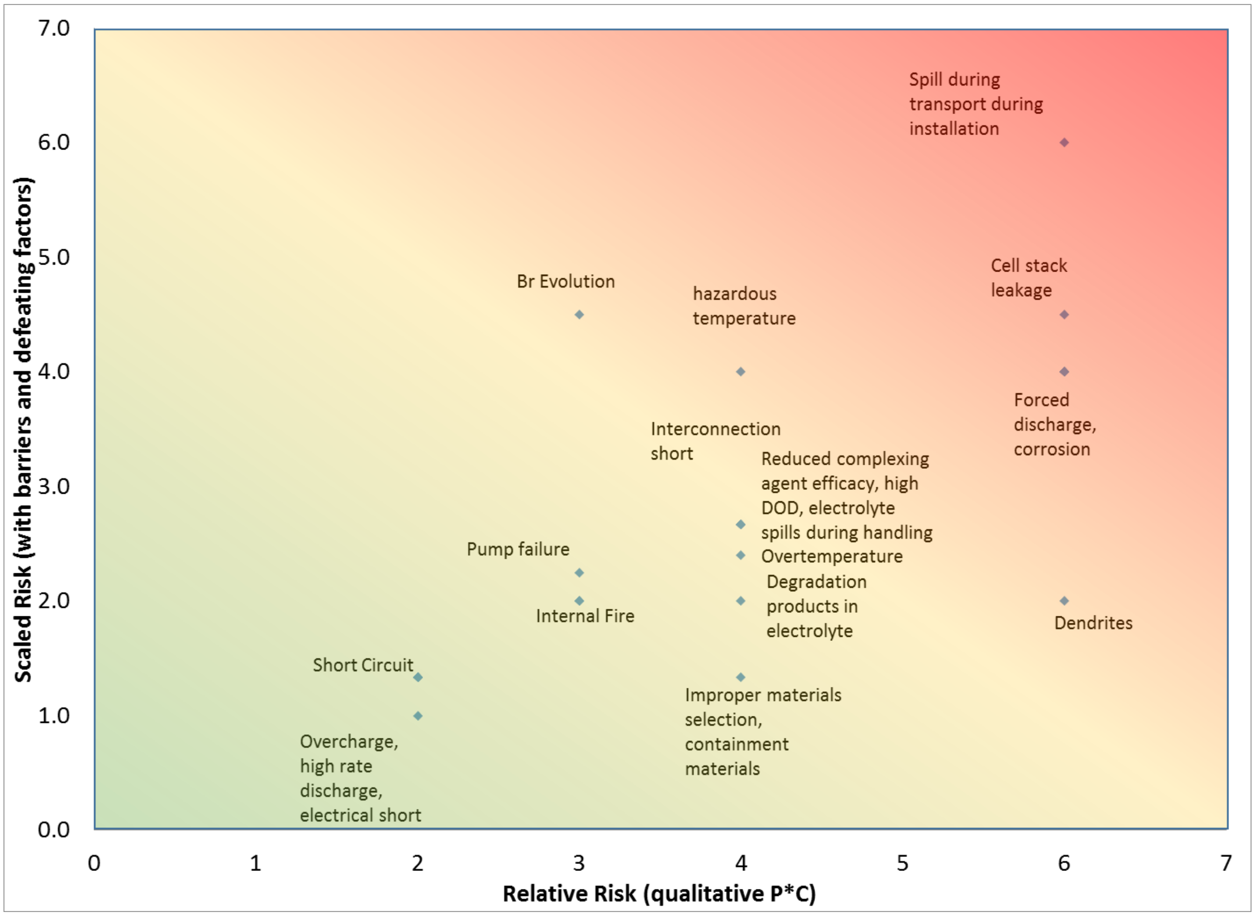


Figure 11 Risk chart.

5 COMPARISON OF PERFORMANCE AND SAFETY TO OTHER TECHNOLOGIES

There are a range of electrochemical energy storage technologies, but each technology tends to be strong in one or two categories with some tradeoff in the others.

5.1 Performance Comparisons

Due to thermodynamics and electrochemical equilibrium factors, the following performance relationships are inversely proportional:

- High power technologies are generally lower energy technologies
- High energy technologies are generally lower power technologies

- Long discharge technologies are generally low power, and perhaps low efficiency
- Short discharge duration technologies are generally high power technologies

Power Density

In Figure 12 it is shown that Zn-Br flow batteries have relatively low power density compared to other battery technologies. Some Pb-acid batteries meant for long discharge are equivalent or lower power density.

Discharge Time

In Figure 13 it is shown that Zn-Br batteries have the capability to perform long discharges for 2 or more hours, which exceeds most Li-ion batteries and is competitive with Pb-acid batteries.

Energy Density

In Figure 14 it is shown that Zn-Br flow batteries have relatively low energy density compared to Li ion batteries, though they may be close to the LTO (Li-ion titanate) chemistries made by Toshiba and Altairnano. There are some Pb-acid batteries with lower energy density.

Combined Factors

In Figure 15 it is shown that ZnBr flow batteries are in the lower left quadrant of the Power vs. Energy density chart, near Pb-acid and other flow battery technologies. In general it is seen from these comparisons that ZnBr flow batteries have strength in their long discharge duration which may make them ideal for peak shaving or backup applications, though in those applications the lower energy and power density may require that large or stacked systems may be needed. For example, Li-ion is capable of multi hour discharge if performed at C-rates less than 1. Thus the flexibility of Li-ion is that it can be used for long discharge at a derated power, or can achieve high power or energy if needed as well.

These figures do not account for cost or longevity. In this study both of these factors have not been assessed, but a long discharge, long life, low cost battery can overcome its flexibility limitations if it is aptly suited to an optimized application. It has been claimed that ZnBr flow batteries are low cost in comparison to other chemistries, though that claim has not been validated in this study.

5.2 Safety Comparisons

Li-ion batteries offer higher power density at the tradeoff of thermal runaway risk. In a fire, Li-ion batteries can emit toxic chemicals. Zn-Br batteries, in contrast, do not have a thermal runaway risk but in a fire can potentially evolve bromine gas. Other Li-ion variants such as $LiFePO_4$ and Li-titanate chemistries can offer high power with low thermal runaway risk, at the compromise of energy density. Pb-acid batteries offer long discharge duration at the expense of low energy and power density. Pb-acid batteries have well understood safety risks including evolution of hydrogen, and handling or disposal of their acidic electrolytes. The qualitative comparison of safety issues for Zn-Br vs. Li-ion is shown in Figure 16. While it can be seen that there are more high level safety issues (by number) for Li-ion in this limited list, there are still high risks for both, with different probabilities and consequences. The figure (Figure 16) should be explained with plenty of caveats, as it is not a comprehensive safety comparison but is instead a normalized ranking of safety issues from 2-3 energy storage devices compared side by side. Therefore there are contextual considerations. What can be seen is that forced discharge is a hazard for both Li-ion and Zn-Br. The safeguards in the Li-ion systems make this risk relatively low, while it is higher for Zn-Br on a relative scale. The same is true for over discharge. The short circuit risk is also present for both technologies, with a slightly greater risk for Li-ion. Electrical system or EMC failures are common to both and are ranked in generally the same risk range. External fire is a high risk that is common to both, but for different reasons. An external fire can create Bromine gas for Zn-Br batteries, and create a thermal runaway risk for Li-ion batteries. The main takeaway is that an external fire is an unacceptable risk for any battery considered here. Internal fires are also risks for both systems. HVAC failure is a unique risk for Li-ion but it was identified that most Zn-Br systems do not have HVAC. Finally, cell stack leakage and electrolyte spills are a unique risk for Zn-Br that is not present with Li-ion. Conversely, cold temperatures are a potential hazard to Li-ion batteries yet this does not pose a significant known safety risk for Zn-Br.

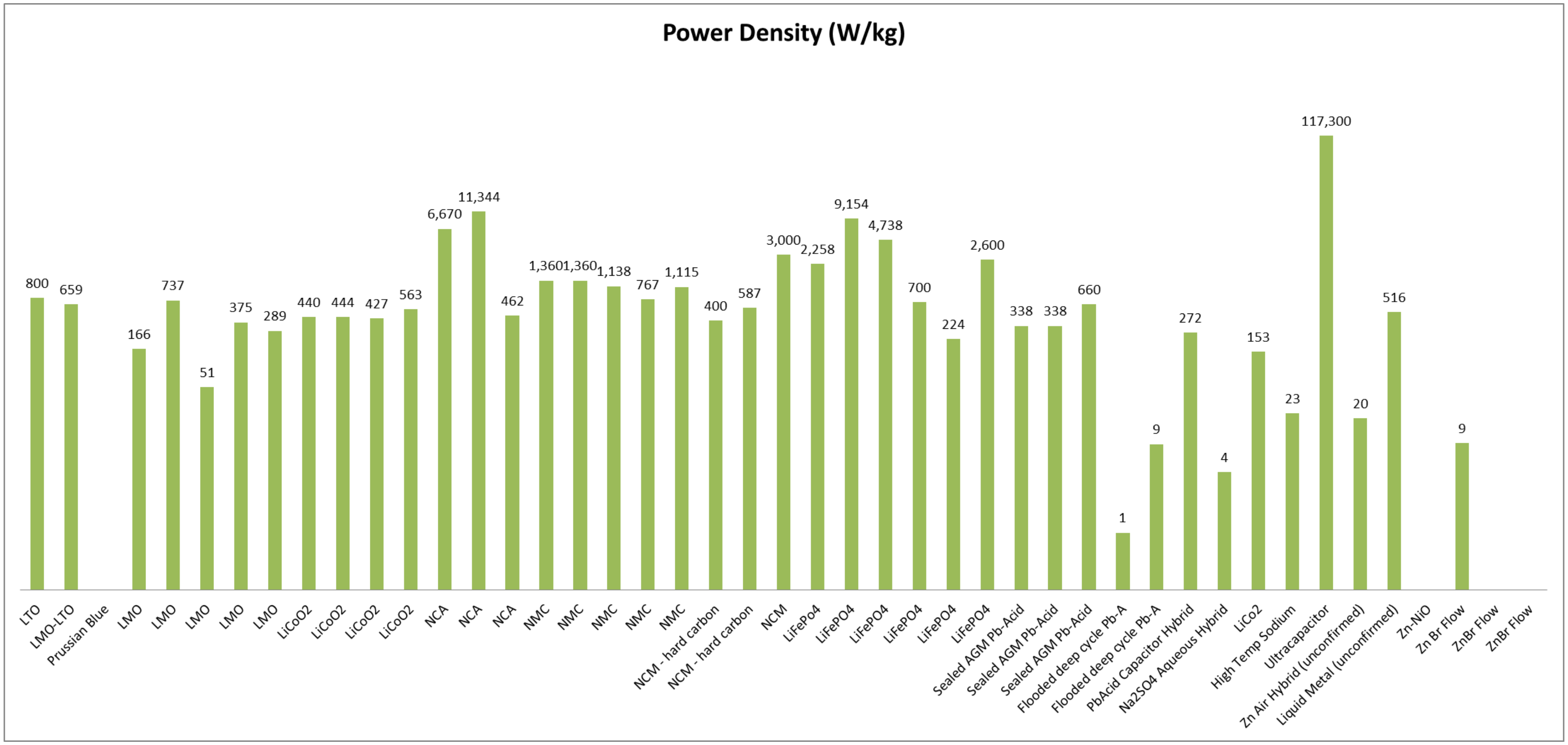


Figure 12 Comparison of power density for Zn-Br battery types against many other chemistries.

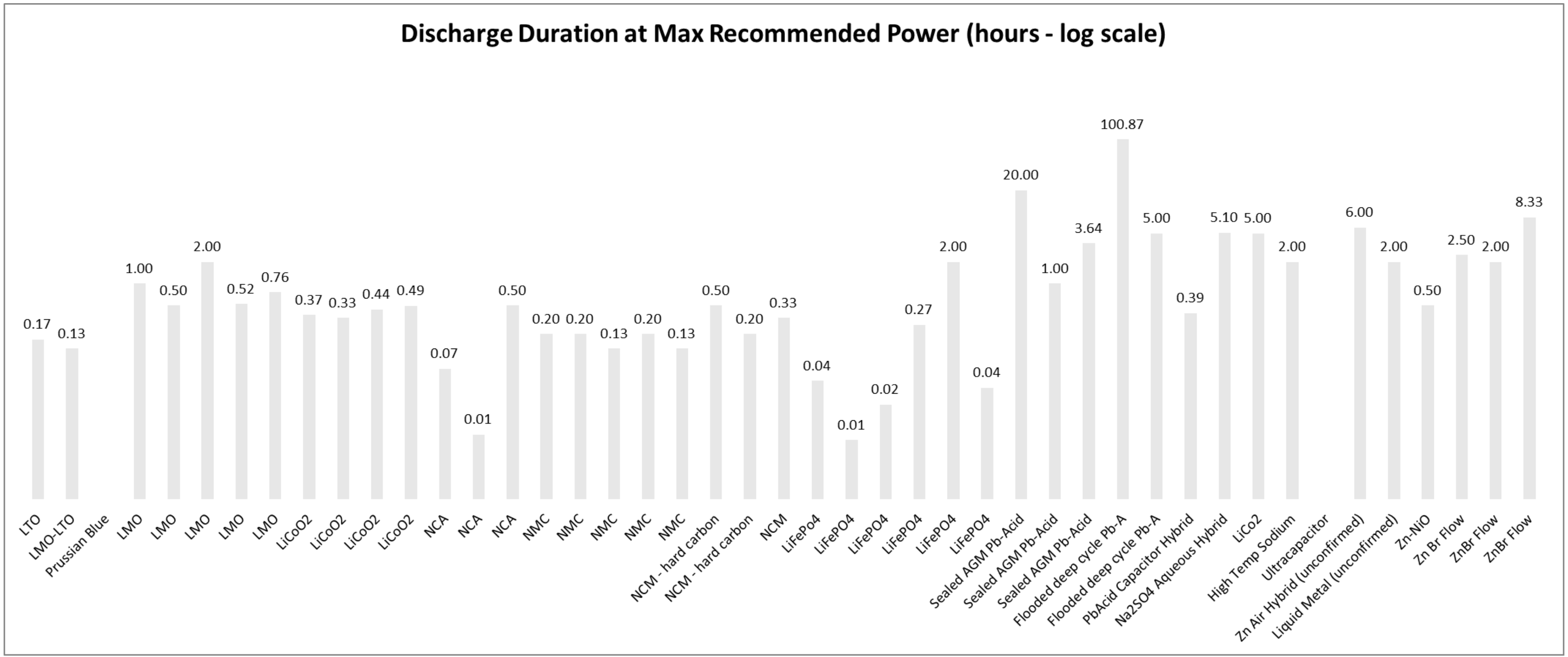


Figure 13 Comparison of discharge duration of ZnBr battery types against many other chemistries.

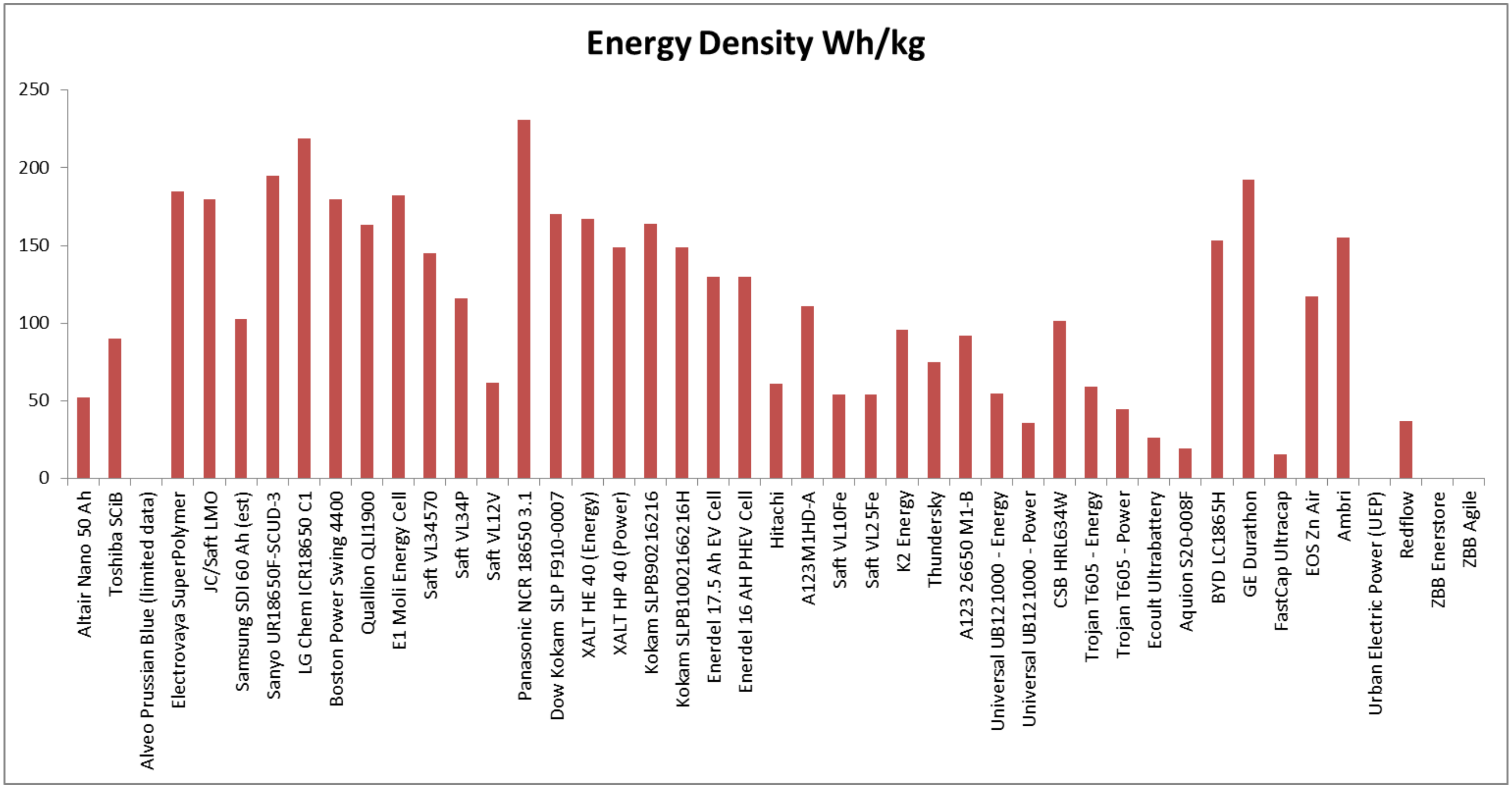


Figure 14 Energy density for multiple battery chemistries (zero values are incomplete datasets).

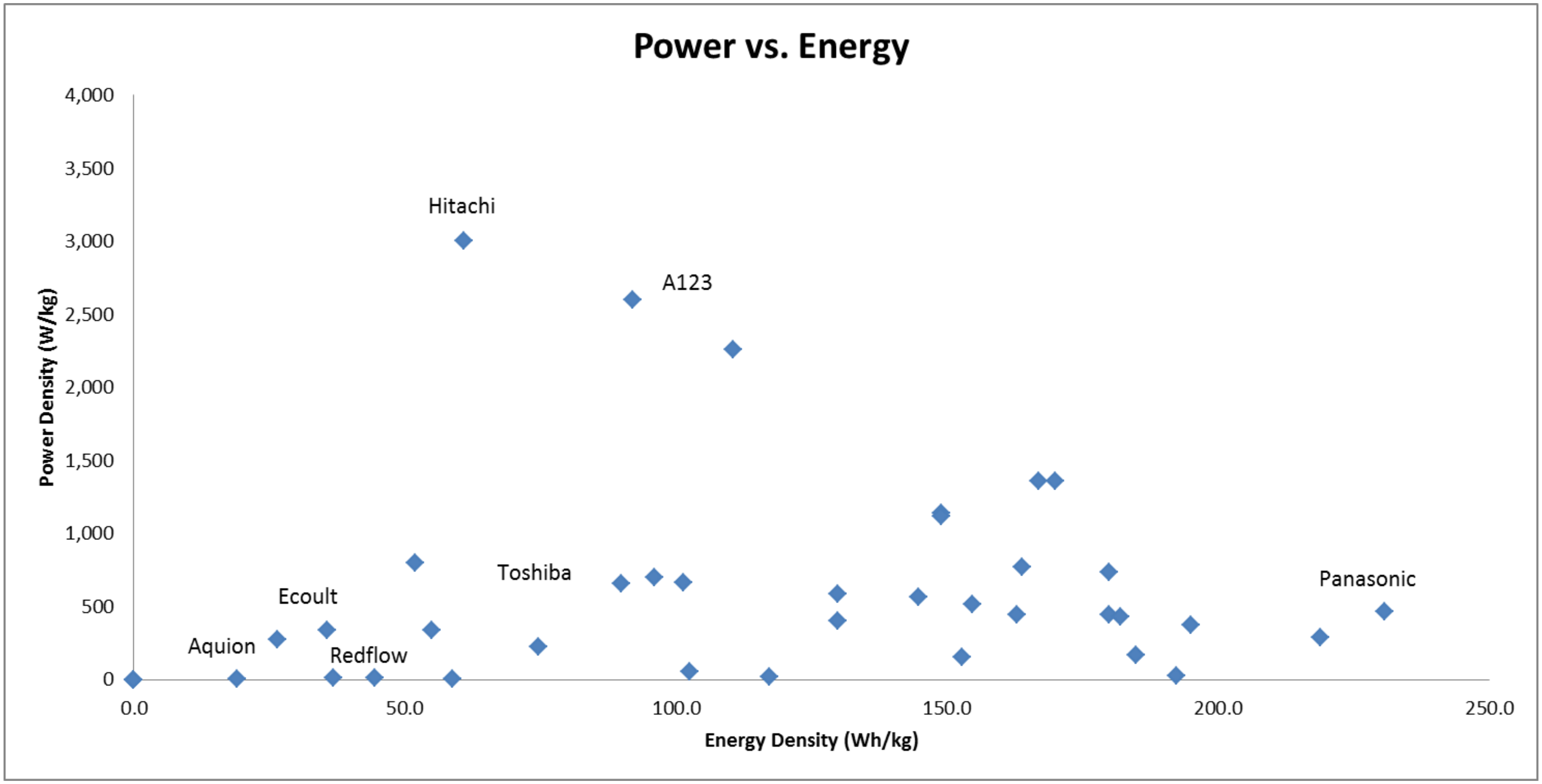


Figure 15 Power vs energy density for multiple battery chemistries.

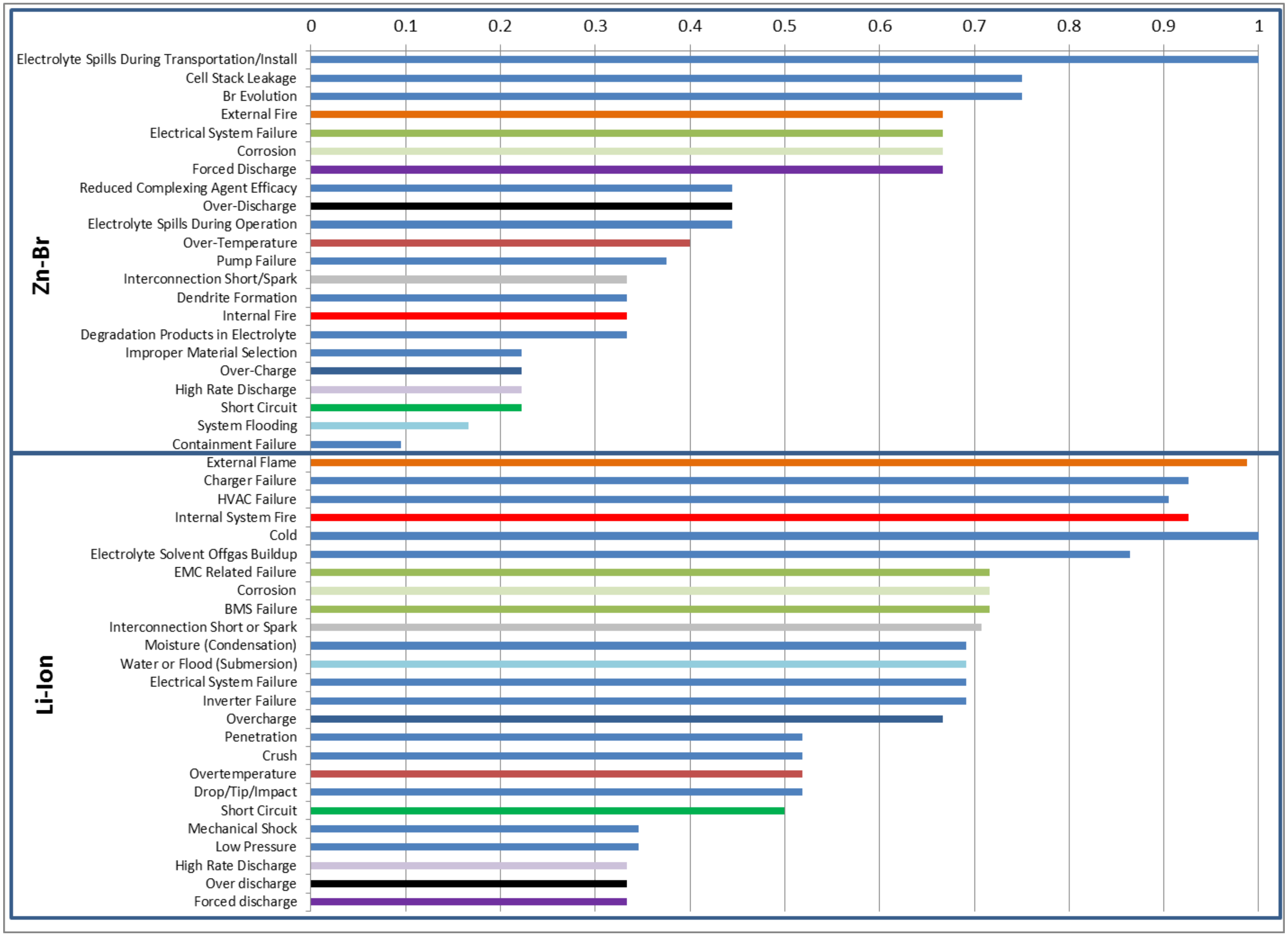


Figure 16 Relative severity of safety issues for Zn-Br vs. Li-ion.

6 SUMMARY OF KEY FINDINGS

DNV GL identified the following findings:

- Most manufacturers do not use automated fire suppression systems
- Some manufacturers do not use HVAC control in the system
- The complexing agent appears to be stable as long as temperatures do not climb > 50°C which may provide a 5°C safety margin
- Contaminant materials from the ambient environment to degrade complexing agents have not yet been identified
- Materials selection issues in the industry are creating more barriers to cell stack leakage

It should be noted that the responsible parties for the risks identified may be closer to the installers, system integrators, or end users at the site. Issues such as containment failure, if created due to third party damage, are out of the hands of the battery manufacturer.

- *Electrolyte spills during transport/Install* - The battery manufacturer has less control over this than it does during the electrolyte filling process at the manufacturing factory, especially if the manufacturer is not involved with the installation or any additional transport of batteries after initial delivery. Thus there is a need for training for proper handling to freight companies and drivers, but battery tank. Battery electrolyte tank design, however, would be something that is within the sphere of control for battery manufacturers.
- *External Fire* –The battery manufacturer has less control over this especially when installing batteries through third party system integrator or installer companies. Appropriate education for these third party companies is important to ensure the risks associated with external fires are understood, and sufficient measures to mitigate these risks are taken. These system integrators will determine if a fire suppression system is installed and may make the applications or approvals to the site authorities having jurisdiction (AHJs). Or, the system integrator may rely upon extinguishers already at the site. In many cases it may be necessary to evaluate the appropriateness of such decisions.
- *Containment Failure* –Protection against impact should be considered by the system integrator and/or system installer, as well as the battery manufacturer.

From the above considerations, it can be seen that there is a disconnect and/or liability transfer between the battery manufacturer and system integrator. For issues like fire suppression, each party may refer to the other for responsibility of incorporating it. It is the same for HVAC systems.

7 RECOMMENDATIONS

As a result of these findings DNV GL recommends the following:

- The use of HVAC or fire suppression would add barriers to prevent over-temperature events that could create a > 50°C environment. This may also be accommodated by system shutdown, provided that external heat factors are not present that an HVAC system would otherwise counteract.
- In populated areas, preventions for impact should be included, such as fenced or limited access areas
- In evaluation of whether HVAC or fire suppression should be used, a multi-stakeholder discussion is necessary in order to determine if the integration of such systems is the responsibility of the battery manufacturer, system integrator, or site owner. Such processes may include an interactive FMEA or HAZID process with a moderating party.
- Considerations for the fire suppression and ventilation within the building where the ESS unit is housed may also be a consideration.

8 REFERENCES

1. Handbook of Battery Materials, edited by Claus Daniel, J. O. Besenhard, Second Edition, Wiley (2011).
2. Eidler, Phillip. Development of Zinc/Bromine Batteries for Load-Leveling Applications: Phase 1 Final Report. Sandia National Laboratories, operated for the United States Department of Energy. 1999.
3. Qi Qu, Paul Javora, Joel Boles, and Sandra Berry. Method of Reclaiming Brine Solutions Using an Organic Chelant. Qi Qu, assignee. Patent US 20070095762 A1. 3 May 2007.
4. Jay P. Deville, Matthew L. Miller, Stephen W. Almond, Douglas J. Harrison. Method of Removing Metal Contaminants from High-Density Brines. Halliburton Energy Services, Inc., assignee. Patent US 20110062085 A1. 17 March 2011.
5. Paul C. Butler, Phillip A. Eidler, Patrick G. Grimes, Sandra E. Klassen, and Ronald C. Miles, Advanced Battery Systems, Chapter 37: Zinc / Bromine Batteries, SAND2000-0893.
6. C Menictas, M Skyllas-Kazacos, T M Lim, Advances in Batteries for Medium and Large-Scale Energy Storage, Elsevier (2015).
7. M. Skyllas-Kazacos, M. H. Chakrabarti, S. A. Hajimolana, F. S. Mjalli and M. Saleem, Journal of The Electrochemical Society, 158 (8) 1-25 (2011).

9 APPENDIX:

9.1 Br-Based Energy Storage Technologies

Bromine and its bromide derivatives are used in several electrochemical energy storage technologies. These may include the following established and emerging storage technologies:

- Zn-Br flow batteries
- Hydrobromic Acid battery (liquid bromine + hydrobromic acid)
- Polysulfide bromide batteries (PSB)

A few examples of relevant companies and technologies that may benefit from ICL's Bromine production are:

- ZBB Energy Corporation (Zn-Br)
- RedFlow Limited (Zn-Br)
- Primus Power (Zn-Br)
- EOS Energy Storage (Zn-Br hybrid)
- Regenesys[4] (PSB) and related technologies

The zinc-bromide battery has a typical energy density ranging between 30-50 Wh/kg, which is about 25-30% of the energy density of Li-ion, about 2-3x the energy density of modern ultracapacitors, and is nearly equivalent to deep cycle Pb-acid (AGM and VRLA) batteries. The claimed advantages of Zn-Br flow batteries include high cycle life (~2000 cycles or more), large state of charge (SOC) swing or 100% depth of discharge (DOD) capability, long calendar lifetimes, high scalability making them relevant for grid-scale energy storage. Their capital cost is also claimed to be competitive with Li-ion and other technologies. [5]

Realizing the opportunities that exist for innovative electrical energy storage, ICL-IP has begun proactive initiatives to support this emerging market. These activities include the operation of an electrochemical laboratory in support of developmental activities in bromine-based energy storage solutions. ICL provides advice and technical support derived from their experience in bromine handling and wishes to enhance this support by offering further services in complexant development, construction materials, and materials safety. ICL has recruited DNV GL for assistance in the materials safety efforts, beginning with a safety review spanning the production, distribution, and integration of Br into electrochemical energy storage systems.

9.2 Bromine Safety and Handling[6]

While the scope of this work is focused on bromine-based electrolytes and pure bromine is not likely part of the energy storage market considered here, there are still some basic safety and chemical property considerations for this market that will

---

[4] No longer in operation

[5] Bradbury, Kyle. "Energy Storage Technology Review", Duke Energy. August, 2010.

[6] Bromine MSDS, Science Lab.com, Inc. 14025 Smith Rd, Houston TX 77396

be relevant to ICL and the target customers. At standard temperature and pressure (STP) Bromine is liquid. It is a halogen with atomic number 35, and has an atomic weight of 79.9 g/mol. Bromine is semi-stable as a diatomic liquid, Br_2. It is about 3x as dense as water (3.1 g/cm^3) and has a vapor pressure of 10,000 Pa near room temperature (~ 3x that of water) meaning it is in an evaporative state at STP. Its boiling point is 58°C. [7] Bromine does have reasonable solubility in water but is highly soluble in organic solvents such as some alcohols and acetic acid. Br_2 is not flammable and thus has no auto-ignition or flash point considerations. There is no mentioned risk of explosion risk associated with impact or crush of containment vessels.

Bromine has a high electronegativity (between 2.8-2.9 on the Pauling scale, 4th highest in the periodic table), meaning that it is less volatile than Chlorine but more volatile than Sulfur. The above considerations are for pure bromine. Bromine-based electrolytes, however, may be more inert. The corrosivity and toxicity of bromine would arise if bromine-based electrolytes are spilled, heated, evaporated, or otherwise reacted to liberate bromine.

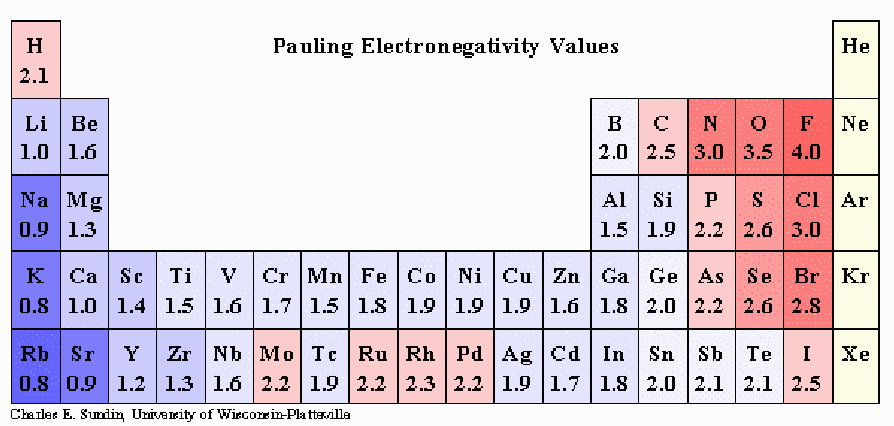
9.3 Human Exposure

Again, it is assumed that bromine-based electrolytes will be more inert than pure bromine. Human exposure considerations would arise if bromine is liberated from its bromine-based electrolyte compounds. Most of the human factor hazards associated with Br_2 are associated with liquid or gaseous exposure. The odor threshold for Br is 0.05 ppm. Bromine is hazardous to humans with regard to skin contact, eye contact, ingestion, or inhalation. Human exposure to Br_2 vapor may cause damage to mucous membranes of the eyes, mouth, and respiratory tract. Inhalation of a spray mist may produce severe irritation characterized by coughing, choking, or shortness of breath. Severe over-exposure may result in death. In most cases for minor skin exposure, treatment washing with warm water is recommended. Damaged skin may include ulceration and burns, and should be covered with emollient or anti-bacterial cream. For inhalation, fresh air and/or artificial respiration are needed. If ingested, induced vomiting is not recommended. Exhaust ventilation is recommended in stored areas. Use face shield and full suit when working with large volumes of liquid bromine. Exposure Limits:

- Time weighted average (TWA) = 0.1-0.66 (mg/m^3)
- Short term exposure limit (STEL) = 0.1-0.3 ppm

---

[7] Perry's Chemical Engineer's Handbook, 7th ed. Perry, Green. 1997.



Pauling Electronegativity Values

H 2.1																	He
Li 1.0	Be 1.6											B 2.0	C 2.5	N 3.0	O 3.5	F 4.0	Ne
Na 0.9	Mg 1.3											Al 1.5	Si 1.9	P 2.2	S 2.6	Cl 3.0	Ar
K 0.8	Ca 1.0	Sc 1.4	Ti 1.5	V 1.6	Cr 1.7	Mn 1.5	Fe 1.8	Co 1.9	Ni 1.9	Cu 1.9	Zn 1.6	Ga 1.8	Ge 2.0	As 2.2	Se 2.6	Br 2.8	Kr
Rb 0.8	Sr 0.9	Y 1.2	Zr 1.3	Nb 1.6	Mo 2.2	Tc 1.9	Ru 2.2	Rh 2.3	Pd 2.2	Ag 1.9	Cd 1.7	In 1.8	Sn 2.0	Sb 2.1	Te 2.1	I 2.5	Xe

Charles E. Sundin, University of Wisconsin-Platteville

Figure 1. Relative electronegativity rating of Br compared to all elements in the periodic table.

Br may be considered least electronegative out of the volatile threesome of F, Cl, and Br.
While N and O are more electronegative than Br, they are more stable and inert at STP and less toxic. Thus its electronegativity, corrosivity, toxicity, and high vapor pressure at STP contribute to special safety considerations.

9.4 Flammability and Evaporation Risk

While not flammable under auto-ignition considerations, bromine has some flammability risk in the form of liquid or vapor by spontaneous chemical reaction reducing agents, i.e., when reactions take place that reduce Br_2 to bromides. In the production of Bromine, Chlorine oxidizes the bromide ions to bromine (bromine is reduced). The fire risk is a consequence of contact with flammable materials during these reactions, such as sawdust, metal dust, cotton, straw, etc. Bromine combines readily with potassium, phosphorus and tin, and these reactions may be accompanied with spontaneous ignition. Bromine reacts explosively with acetylene, ammonia, hydrogen, sodium, and phosphorus, among others. These reactions may also be relevant to bromine-based electrolytes and may again pose the hazard of liberating bromine from the compounds present in bromine-based electrolytes.

9.5 Spills

Most recommendations for cleanup of a Br_2 spill include absorption with inert materials and corrosive waste disposal. Absorption materials include dry earth, sand, or non-combustible materials. Water spray may be used to dilute and reduce vapors. Containment with dikes recommended for large spills. Never add water to the product, and store in cool, dry, protected areas. In case of a large spill, first responders should be fully suited with respirators and gloves, with likely use of SCBA (self-contained breathing apparatus). In general, the long term degradation products are regarded as less toxic than the product itself. The mostly likely hazard to consider for spills of bromine-based electrolytes is the potential for heating, reaction, evaporation, or other mechanisms of liberation of bromine from compounds in bromine-based electrolytes.

9.6 Containment Materials

Bromine is corrosive to Al, Zn, stainless steel (304 and 316), bronze, and copper. Vessels may be glass lined or plastic, such as polyethylene. Reactive with organic compounds containing hydrogen adjacent to carbonyl group. Br2 is classified as Class 8: Corrosive Material and Calls 6.1: Poisonous material. Bromine based electrolytes may have similar corrosive properties and considerations.

9.7 Complexing Agents and the Electrolyte[8]

Complexing agents are highly relevant to the functionality of the Zn Br battery. A key issue in the safe operation of Zn-Br batteries is avoidance of elevated temperatures > 50oC which may cause Br evaporation. Chemical phenomena that may degrade the functionality of the complexing agent are not readily apparent – though the temperature risk appears to be most relevant. If temperature rises, there is an increased vapor pressure of Br. The operation of the basic Zn-Br flow system is shown in Figure 17. It should be noted in the figure that the Br2 complex decreases with discharge and a pump that only operates on discharge is used to cycle the solution with the complexing agent.

---

[8] Also see "Bromine Complexing Agents" on page 22

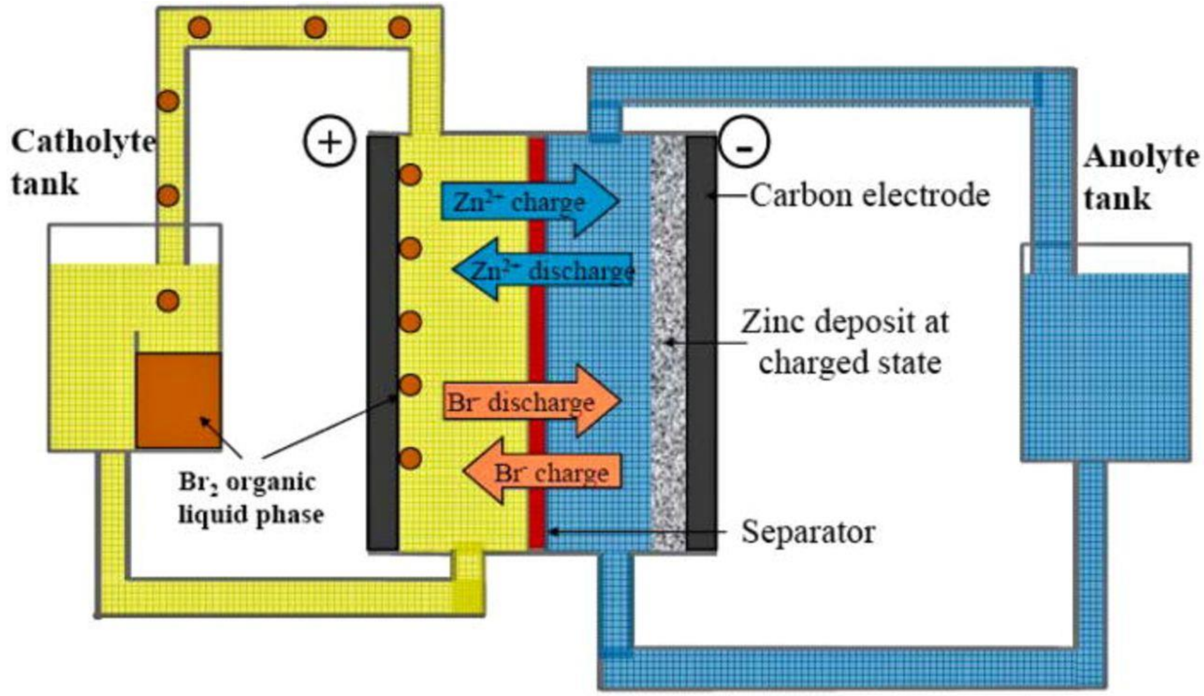


Figure 17 Simplified diagram indicating function of ZnBr systems **(M. Skyllas-Kazacos, 2011)**.

During the charging process, zinc ions are deposited as metallic zinc on the cathode, usually made of carbon.

Zn2+ + 2e- → Zn(s) at cathode / -*v*e electrode

A microporous separator (membrane) differentiates the cathode/catholyte and anode/anolyte compartment to minimize mixing of solutions near cathode and anode, more importantly minimizing diffusion of Br2 or Br2 complex to the zinc cathode for self-discharge that causes losses. Bromide ions (Br-) move from cathode to anode and Zinc ions (Zn2+) move from the anode to the cathode across the separator membrane to maintain charge neutrality in the solution.

At the anode during charging, 2Br- → 2e- + Br2(aq)

The complexing agent holds on to the aqueous bromine to limit its concentration is aqueous form. Circulation of the electrolyte reduces the tendency for zinc dendrites to form and simplifies thermal management of the battery. During discharge, the deposited zinc metal electrochemically dissolves in solution at the cathode, Zn (s) → Zn2+ + 2e-

Bromine is converted to bromide ions at the anode.

Br2 +2e- → 2Br-

The ions in solution move across the separator to maintain charge neutrality. The various elements of the flow battery are considered in detail below, specifically looking as safety aspects associated with each of those components.

9.8 Changes in Concentration of Complexing Agent

The polybromide ions (Br_2 can complex with Br^- in solution to form polybromide ions such as Br_3^-, Br_5^-) are stabilized by reaction with the complexing agent which stabilizes Br_2(aq) disallowing its escape or vaporization, and also forming a second low-solubility liquid phase after complexation that is separated and stored for use during discharge (Paul C. Butler, SAND2000-0893). The complex reduces the amount of bromine contained in the aqueous phase 10-100-fold, which, in addition to the separator, also reduces the amount of bromine available in the cell for the self-discharge reaction. Salts with organic cations such as N-methyl-N-ethylmorpholinium bromide (MEMBr) are commonly used as the completing agents. Complexes with these ions are reversible and also have an added safety benefit due to a much reduced bromine vapor pressure. On charge, circulation of the electrolyte removes the complexed polybromide as it is formed, and on discharge complexed polybromide is delivered to the electrode surface. However, all of these salts, unless used in suitable combinations with other components, allow formation of crystallite structure of the salts and the zinc bromides, which would ultimately short out the flow batteries if costly, time-consuming maintenance procedures are not performed. Commonly utilized classes of quaternary ammonium salts are dialkylpyrrolidinium halides, dialkylmorpholinium halides, and dialkylpiperdinium halides, including, e.g .methylethylpyrrolidiniutn bromide "MEP" and methylethylmorpholinium bromide "MEM" (C Menictas, 2015).

Desired properties of complexing agents are the following:

- Should not crystallize at 0-50^0 C, essential for operation without shorting.
- Sufficiently high densities of the fused state (Br^{2+} salt) for ease of separation of complex phase from aqueous phase
- To ensure low self-discharge, complex with Br_2 for substantial reduction in equilibrium vapor pressure of Br_2 of the polybromide phase in association with low solubility of active bromine in the aqueous phase
- A mixture of quarternary ammonium salts rather than one single salt is used to meet these requirements

- Quantitative assessment of complexing agent effects on kinetics etc. of battery operation are not available

	Other Queries on Complexing agents	Literature	Safety Threat
1	Can these decompose to harmful substances at or above 60°C?	No literature found, no negative effects of complexing agent degradation discussed (Claus Daniel, 2011)	Not existent within 0°C to 50°C, Br may boil at higher temp
2	Loss of ability of hold on to Bromine as it ages/ used over extended cycles	Not observed	Not a significant threat

9.9 Electrolyte Re-use and Transition Metal Salts as Impurities in the Electrolyte

A possibility of existence of transition metal ions (ions or salts of Fe, Pb, Ag, Cd, Cu etc.) was explored. General search, as well as academic journal search revealed that this is not a common occurrence with $ZnBr_2$ flow batteries. Low ppm levels of most of the transition metals is a quality issue to maintain recycle performance after many charge / discharge cycles. The source of these metal ions could be corrosion of metal components over time.

One patent (“*Ultra-high purity zinc bromides and quaternary ammonium bromides for use in zinc-bromine batteries WO 2008109232 A1”* Albemarle Corporation (Chemical Manufacturer), Joe D Sauer, George W Cook Jr) discusses source of transition metals as impurities in either Zn or Br liquid, used to form $ZnBr_2$, suggests ways to form electrolyte with <1ppm level impurities from transition metals or their salts. They have developed a method for producing ultra-high purity zinc bromide by reacting an excess of zinc metal with a limited amount of elemental bromine. Such a reaction leaves a heel of zinc metal that also contains the metal impurities introduced in the feedstock zinc with the soluble zinc bromide being isolable in highly pure form. As an additional benefit, this process also improves the quality of the quaternary ammonium bromide present in the system in that any impurities present therein stay in the unreacted zinc metal.

The Zn-Br electrolyte formulation can nominally be recycled for the life of the fuel cell, and likely beyond. The compound does not break down over time, although it is susceptible to contamination by foreign materials. Contamination may originate from stack corrosion, or external factors due to handling and transportation. The primary tasks of recycling an electrolyte are analysis for purity and composition, treatment to reduce transition metals, and filtration. The two main analytical tools required for such a process are thus an inductively coupled plasma (ICP) analyzer for determining ppm levels of metals and an ion chromatograph for doing composition/concentration analysis of the electrolyte. (Eidler 1999)

Contaminated electrolyte must be processed before re-use. One such method involves using powdered zinc to precipitate foreign metals, which may then be filtered to remove the precipitates. Many of these reprocessing methods derive from the Oil Drilling industry where ZnBr has been used as a completion fluid for tens of years. Most contaminants can be removed through a simple filtration process; such as a plate and frame type filter and then through a cartridge polishing filter (Qu 2007, Deville 2011). Though effective at particulate filtration, these methods are not able to remove other types of contamination such as colloidal or soluble species.

Iron is a typical contaminant found in used completion fluids that is particularly difficult to remove from zinc-containing, high-density brines. The relatively low pH of ZnBr, as well as the fact that iron is likely to be in a soluble and stable form, make it a particularly difficult to remove. Since oxygen has a low solubility in such solutions, a significant amount of the iron contaminants will exist as ferrous iron. Thus, precipitation of the iron hydroxide via calcium hydroxide, calcium oxide, or other common compounds is ineffective because of zinc hydroxide complexes which make it virtually impossible to raise the pH significantly. Adding lime or other materials can still be an important step in the reclamation process, though the pH of such zinc-containing fluids cannot be raised above 6.0. Still, several processes have been developed for removing iron contaminations: (Qu 2007, Deville 2011)

- One ZnBr reclamation process consists of the oxidation of polymeric species to reduce the viscosity and yield point of the contaminated brine, oxidation of Fe^{2+} to Fe^{3+} to facilitate removal of iron, and the oxidation of organic species which interfere with the reclamation process.
- Another process consists of the initial filtration of the brine followed by a reduction in the pH of the brine fluid. Carbon or bentonite absorbent is then added to the brine and the solution is allowed to stand for about six hours. The resulting solids are then filtered and the pH of the resulting system is slowly raised. The fluid is then re-filtered and tested for compatibility.
- Yet another multi-step reclamation process, the spent brine is mixed with acid in order to lower the pH. The fluid is then contacted with a halogen, such as bromine, to increase the density. A reducing agent, such as anhydrous ammonia, is then added. An alkali is then used to neutralize any excess acid. Finally any suspended solid impurities are removed.

9.10 Electrodes

Graphitic or vitreous carbon materials are widely used in RFBs, such as graphite, carbon felt, carbon fiber, thermal and acid treated graphite, carbonpolymer composite materials, carbon nanotubes, IR-modified carbon felt and graphene-oxide nanoplatelets. In general, RFB couples are chosen for the facile kinetics so highly active catalytic materials are not necessary. Nonetheless, it has been found that various surface treatments can lead to improved reaction kinetics on carbon electrodes. Chemical etching, thermal treatment, chemical doping, carbon nanotube addition, and addition of metallic catalyst sites to the carbon fibers have all been attempted. Aside from catalytic activity, the main criteria for electrode materials are electrical conductivity, chemical stability and durability in the reaction environment. Carbon and graphite materials meet both these requirements, though metal foams and meshes are also candidates. (M. Skyllas-Kazacos, 2011)

	Queries on Electrodes	Literature	Safety Threat
1	Can these corrode over time?	Yes, they could corrode with time of usage and create debris for the pump to deal with, though such cases are rectified by scheduled maintenance	Not a significant threat
2	Are there metal impurities associated with the electrodes that could lead to transition metal impurities in the electrolyte?	Not observed in literature. Impurities are sourced from the bromine source.	Not a significant threat

9.10.1 Shunt Currents

Cells are connected electrically in series and hydraulically in parallel which lead to alternate pathway for the current through the common electrolyte channels and manifolds during charge, discharge, and at open circuit. Such currents are referred to as shunt currents and cause uneven distribution of zinc between end cells and middle cells. This uneven distribution causes a loss of available capacity because the stack will reach the voltage cutoff upon discharge sooner than if the zinc were evenly distributed. (C Menictas, 2015)

Shunt currents may lead to uneven plating on individual electrodes, especially the terminal electrodes. This uneven plating can in turn lead to zinc deposits that divert or even block the electrolyte flow. Shunt currents can be minimized by designing the cells to make the conductive path through the electrolyte as resistive as possible. This is done by making the feed channels to each cell long and narrow to increase the electrical resistance. This, however, also increases the hydraulic resistance and thus' the pump energy. Good battery design balances these factors. Higher electrolyte resistance reduces shunt currents but also reduces battery power. Since the cell stack voltage is the driving force behind the currents, the number of cells in series can be set low enough that the magnitude of the shunt currents is minimal.

	Queries on shunt currents	Literature	Safety Threat
1	Are they a safety threat?	Can be assessed by cell design, could lead to lowering capacity but not seen as a safety threat – mostly a performance threat	Not a significant threat

9.11 Transport of Bromine-based Electrolytes

Early Zinc-bromine batteries included a plurality of electrodes disposed in a non-flowing, zinc-bromide aqueous solution. Over time zinc-bromine batteries were developed as flowing electrolyte batteries in which the electrolyte is circulated through a stack of electrochemical cells during charging and discharging, and is stored in external reservoirs.

Flowing electrolyte, zinc-bromine batteries have an aqueous solution of zinc-bromide and quaternary ammonium salts, for example, methy-methylpyrrolidinium bromide, with optional supporting salts, such as NH_4Cl, which is circulated through the individual cells from external reservoirs[9].

The most common electrolyte in zinc-bromine batteries is aqueous solution of zinc bromide (**$ZnBr_2$**). The information on ingredients and its physical properties are listed below.

Table 2 $ZnBr_2$ characteristics.

Substances	
Empirical Formula:	$ZnBr_2$ in water
Synonyms:	Zinc dibromide solution in water
Chemical Family:	Inorganic Bromide
Chemical Abstract Service (CAS) Number:	7699-45-8
European Community (EC) number:	231-718-4
Concentration:	<= 100%
Hazardous Classification:	Acute Tox. 4; Skin Corr. 1B; Eye Dam. 1; Skin Sens. 1; Aquatic Acute 2; Aquatic Chronic 2; H302, H314, H317, H318, H411
Appearance:	Clear Colorless Viscous liquid, Irritating, Causes burns
Physical Properties	
Boiling Point:	136°C (250°F)
Freezing Point:	ca -8°C (18°F)
Decomposition Temperature:	690 °C (1274 °F) ($ZnBr_2$ 100%)
Hazardous decomposition products:	Hydrogen bromide and bromine
Molecular Weight:	225.20 g/mol
Vapor pressure:	5.2 mm Hg (25°C)
Solubility in Water:	Soluble
Solubility in other solvents:	Ethanol
Specific gravity:	2.3 - 2.5
Reactivity (materials to avoid):	Metallic sodium and potassium and strong oxidants

---

[9] US Patent US 08/499,144, Phillip A. Eidler, Peter J. Lex, publication number US5591538 A1, Jan 7, 1997.

The hazards identification can be found from the MSDS of zinc bromide (GHS Classification in accordance with 29 CFR 1910 (OSHA HCS)).

Table 3 Toxicity and hazard classifications per OSHA.

Classification	Category	Hazard Statement
Acute toxicity, Oral	4	H302
Skin corrosion	1B	H314
Serious eye damage	1	H318
Skin sensitization	2	H317
Acute aquatic toxicity	2	H401
Chronic aquatic toxicity	2	H411

Table 4 GHS Label Elements, including precautionary statements

Pictogram	 **Corrosion GHS05**  **Exclamation Mark GHS07**  **Environment GHS09**
Signal word	Danger
Hazard statement(s)	
H302	Harmful if swallowed.
H314	Causes severe skin burns and eye damage.
H317	May cause an allergic skin reaction.
H318	Causes serious eye damage.
H401	Toxic to aquatic life
H411	Toxic to aquatic life with long lasting effects.

The transport information of zinc bromide solution can be summarized in Table 5. In Table 6 UN numbers or UN IDs are four-digit numbers that identify hazardous substances, and articles (such as explosives, flammable liquids, toxic substances, etc.) in the framework of international transport. UN numbers range from UN0001 to about UN3518 and are assigned by the United Nations Committee of Experts on the Transport of Dangerous Goods. There is no UN number allocated to non-hazardous substances. These will simply not have a UN number.

- UN 1760 Class 8 Corrosive liquids, n.o.s.
- UN 3260 Class 8 Corrosive solid, acidic, inorganic, n.o.s.

Associated with each UN number is a hazard identifier, which encodes the general hazard class and subdivision.

Table 5 transportation classification requirements

Classification Item	ICL Information	Info from other vendor
US Department of Transportation (DOT)		
UN Number	1760	3260
Class	8	8
Package group	II	III
Proper shipping name	Corrosive Liquid, n.o.s. (contains Zinc bromide)	Corrosive solid, acidic, inorganic, n.o.s. (Zinc bromide)
Reportable Quantity (RQ)	1000 lbs	1000 lbs
Marine pollutant	Yes	Yes
Poison Inhalation Hazard	N/A	No
International Maritime Dangerous Goods Code (IMDGC)		
UN Number	1760	3260
Class	8	8
Package group	II	III
IMO Proper shipping name:	Corrosive Liquid, n.o.s. (contains Zinc bromide)	CORROSIVE SOLID, ACIDIC, INORGANIC, N.O.S. (Zinc bromide)
Marine pollutant	Yes	Yes
EMS (Emergency Schedule)	F-A, S-B	F-A, S-B
International Air Transport Association (IATA)		
UN Number	1760	3260
Class	8	8
Package group	II	III
IMO Proper shipping name:	Corrosive Liquid, n.o.s. (contains Zinc bromide)	Corrosive solid, acidic, inorganic, n.o.s. (Zinc bromide)
Marking	Environmentally hazardous substance	N/A
Transportable quantities	Can be transported by air but quantities are limited to 1 liter on passenger aircraft and 30 liters on cargo aircraft	N/A

Table 6 Hazard classes for hazardous chemicals in transport.

Class	Description
Class 1	Explosives
Class 2	Gases
Class 3	Flammable liquids (and Combustible liquids [U.S.])
Class 4	Flammable solids; Spontaneously combustible materials; and Dangerous when wet materials/Water-reactive substances
Class 5	Oxidizing substances and Organic peroxides
Class 6	Toxic (poisonous) substances and Infectious substances

Class 7	Radioactive materials
Class 8	Corrosive substances
Class 9	Miscellaneous hazardous materials/Products, Substances, or Organisms

Packing groups are used for the purpose of determining the degree of protective packaging required for Dangerous Goods during transportation.

- Group I: great danger, and most protective packaging required. Some combinations of different classes of dangerous goods on the same vehicle or in the same container are forbidden if one of the goods is Group I.
- Group II: medium danger
- Group III: least danger among regulated goods, and least protective packaging within the transportation requirement

Class 8 Packing Groups

- Packing Group I – Material that causes full thickness destruction of intact skin tissue within 60 minutes, starting after an exposure time of three minutes or less.
- Packing Group II – Material that causes full thickness destruction of intact skin tissue within 14 days starting after an exposure time of more than three minutes but not more than 60 minutes.
- Packing Group III – Material that cause full thickness destruction of intact skin tissue within an observation period of up to 14 days starting after the exposure time of more than 60 minutes but not more than 4 hours

  Or

  Material that do not cause full thickness destruction of intact skin tissue but exhibit a corrosion rate on steel or aluminum surfaces exceeding 6.25 mm (0.25 inch) a year at a test temperature of 55°C (130°F). For the purpose of testing steel P3 (ISO 9328-1) or a similar type, and for testing aluminum, non-clad types 7075-T6 or AZ5GU-T6 should be used. An acceptable test is described in ASTM G 31-72

9.12 Bromine Complexing Agents

Among the preferred complexing substituents in the practice of the present invention are N-methyl, N-ethyl morpholinium bromide (MEM), N-methyl, N-ethyl pyrrolidinium bromide (MEP), N-methyl, N-ethyl pyrolidinium bromide, N-methyl, N-ethyl piperidinium bromide and mixtures thereof.

Essentially, MEP (and other similar compounds) form a water immiscible complex with free Br during the discharging cycle. This complex settles down to the bottom of the cell, effectively removing free Br from the aqueous phase and increasing the coulombic efficiency of the cell. During the charging cycle, the complex is recirculated within the cell to make Br available at the cathode.

9.12.1 Methyl-Ethyl-Pyrrolidinium Bromide (MEP)

MEM is an effective bromine complexing agent for circulating ZnBr2 rechargeable batteries. During batteries operations so-called “bromine fused salts” – liquid polybromide phases are formed between MEM and Br_2.

Formation of immiscible polybromide complexes lowered bromine concentration in aqueous phase and therefore bromine vapor pressure strongly decreases. As a result of complexation bromine activity is reduced and this lowers the rate of corrosion in the battery. Polybromide complexes can be stored in external storage tanks which significantly decreases rate of battery self-discharge.

Table 7 Polybromide complex hazard identifications.

Substances	
Empirical Formula:	$C_7H_{16}BrN$
Synonyms:	1-Ethyl-1-methylpyrrolidinium bromide
Chemical Family:	Inorganic Bromide
Chemical Abstract Service (CAS) Number:	69227-51-6
European Community (EC) number:	418-200-5
Appearance:	Colorless to slightly yellow liquid with a slight amine odour
Physical Properties	
Boiling Point:	100 °C (212 °F)
Vapor pressure Odorless:	13 mbar @ 20°C
Molecular Weight:	194.11 g/mol
Solubility in Water:	Highly soluble
Solubility in other solvents:	Highly soluble in ZnBr2 solutions, HBr, organic solvents
Specific gravity of 65% aqueous solution:	1.19

9.12.2 Comparison Between ICL and Sigma-Aldrich MSDS

The hazards identification can be found from the MSDS of zinc bromide.

Table 8 Classification of substance mixture **GHS Classification in accordance with 29 CFR 1910 (OSHA HCS)**

Classification	Category	Hazard Statement
Muta. Germ cell mutagenicity	2	H341

Table 9 GHS Label elements, including precautionary statements

Pictogram	 **Health Hazard GHS08**
Signal word	Warning
Hazard statement(s)	
H341	Suspected of causing genetic defects.
Precautionary statement(s)	
P201	Obtain special instructions before use.

P202	Do not handle until all safety precautions have been read and understood.
P281	Use personal protective equipment as required.
P308+P313	If exposed or concerned: get medical advice/attention.
P405	Store locked up.
P501	Dispose of contents/container to an approved waste disposal plant.

The transport information of zinc bromide solution can be summarized as follows.

Classification Item	**ICL Information**	**Info from other vendor**
US Department of Transportation (DOT)		
	Not regulated	Not dangerous goods
International Maritime Dangerous Goods Code (IMDGC)		
	Not regulated	Not dangerous goods
International Air Transport Association (IATA)		
	Not regulated	Not dangerous goods

9.12.3 Methyl-Ethyl-Morpholinium Bromide (MEM)

MEM is an effective bromine complexing agent for circulating ZnBr2 rechargeable batteries.

During batteries operations so-called “bromine fused salts” – liquid polybromide phases are formed between MEM and Br2. Formation of immiscible polybromide complexes lowered bromine concentration in aqueous phase and therefore bromine vapor pressure strongly decreases. As a result of complexation bromine activity is reduced and this lowers the rate of corrosion in the battery. Polybromide complexes can be stored in external storage tanks which significantly decreases rate of battery self-discharge.

Table 10 Properties of polybromide complexes.

Appearance	**Colorless to slightly yellow liquid with a slight amine odour**
Vapour pressure	10.5 mbar @ 20°C
Boiling point/range °C	100°C
Specific gravity of 65% aqueous solution	1.19
Molecular weight	210.11
Solubility:	Highly soluble in water, ZnBr2 solutions, HBr, organic solvents.

9.13 Battery Manufacturer Questionnaire

Thank you for supporting our work with ICL concerning the safety assessment of bromine-based electrolytes for the stationary energy storage sector. We hope that you will not mind taking some time to respond to the following questions, which will help DNV GL fulfill a detailed safety analysis for ICL. The purpose of the information is to inform Bowtie models and FMEA such that the strengths and weaknesses of

ICL's product implementation can be identified. ICL intends to use this information to proactively improve their own processes such that they can best serve their customers.

1. How do you obtain materials from ICL? How are they shipped and stored? How do you store them on your facility?
2. Are the materials "raw" or do you process them into their final form?
3. Explain the production processes you use to integrate bromine-based electrolytes into your battery.
4. Is the flow system closed?
5. What materials do you use to contain the electrolyte?
6. What is the sensitivity of your electrolyte to temperature?
7. What are the degradation factors that affect your electrolyte?
8. What are byproducts of degradation?
9. Are there contaminants or impurities in your electrolyte that affect the function of your system?
10. To your knowledge, how different is the electrolyte composition at end of life compared to beginning of life?
11. When shipping a battery system, is the electrolyte shipped with the battery or is it added at the site?
12. What procedures are used to handle the electrolyte at sites?
13. Have there been incidents with spillage or other loss of containment at your facility? How was it handled?
14. Do you provide recommendations beyond the scope of the MSDS when working with customers?
15. What are frequent questions or concerns from customers?
16. What hazards may affect your system in the field?
17. Are there BMS or electrical system failures that could lead to unwanted reactions in your electrolyte?
18. Are their overcharge or overcurrent situations that could lead to unwanted reactions in your electrolyte?
19. Are there instabilities in your electrolyte that could be affected or created by unwanted electrochemical phenomena?
20. Are there any considerations that this survey may have overlooked?

9.14 Bowtie Model Primer: How to Read and Interpret Bowtie Models

The Bowtie model is a qualitative description of hazard and consequence. At a high level, it can be read as a list of all possible hazards on the left, and all possible consequences on the right, with all possible barriers that may prevent consequences in between. The core of the model is the “top event” which is the undesired event. In this case, the undesired event is any loss of battery control[10].

Elements of the model have default shapes and colors that serve to distinguish them as elemental categories for the model structure. Loosely, from left to right, these elements are as follows (Figure 18):

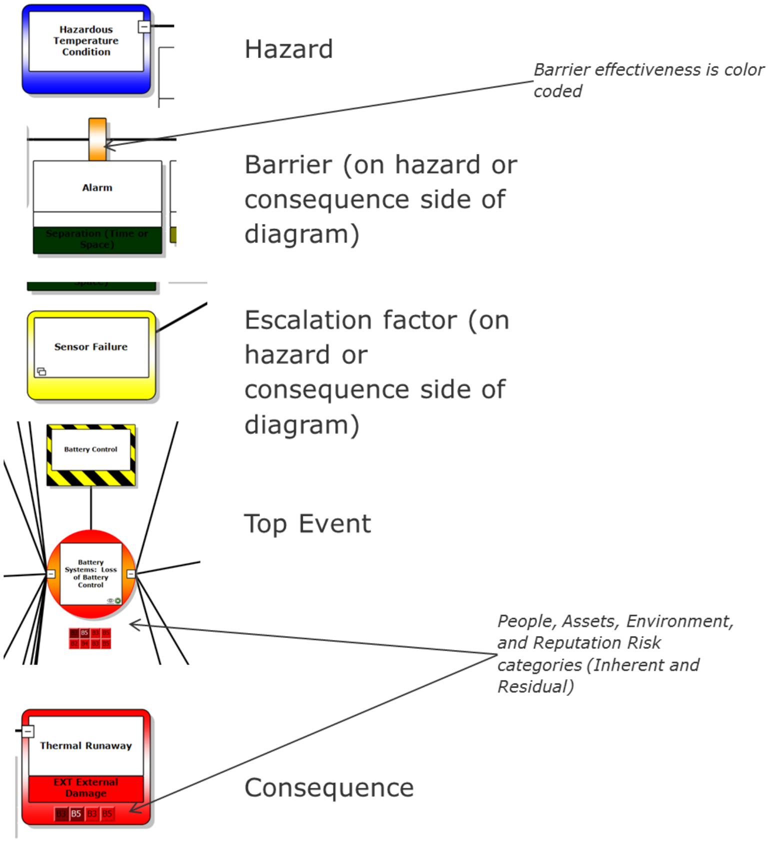


Figure 18 Bowtie model elements explained.

- Hazard (blue boxes)
- Barriers to Top Event (rectangles along the line that connects to the top event)

---

[10] Bowtie XP is commonly used for Hazard and Operability (HAZOP) studies in the oil & gas, chemical, or manufacturing sectors. The context of these analyses is safety risk management, which includes procedures, training, and staff actions to reduce incidents. The analysis includes qualitative probability of an event, which is measured in terms of frequency of those events within a company or industry. There is a means to assign “accountability” to incident categories. For example, this would make sense if there is a Safety, Health, and Environment (SHE) Coordinator within the organization that is responsible for reducing safety incidents on the job. This person would then be named in the “accountable” categories within the Barrier Systems registry. Mitigation or barriers to prevent safety events would likely include training workshops or installation of equipment. Since this project is focused on the operation of equipment and its physical capability to prevent safety incidents, these categories have been ignored.

- Escalation Factors (yellow boxes that connect to barriers)
- Top Event (circle in the center of the diagram with the yellow and black label on top of it)
- Consequence Barriers (rectangles along the path from top event to consequence)
- Mitigation Factors to Consequence Barriers (yellow boxes that connect to barriers, similar to left hand side of diagram)
- Consequences (red boxes)

In general, any path from hazard to consequence is possible. The *Bowtie XP* model should not be interpreted as a prediction that hazard A will always lead to consequence B, but rather *it indicates a possible path with a conditional probability assigned to it*. These diagrams are used to answer questions such as the following:

- Is there a path from the hazard to the consequence?
- What barriers are in place to disrupt this path?
- Are these barriers effective?
- What can be done to improve the effectiveness of these barriers?
- Can we add additional barriers?
- Have we not adequately addressed this hazard?
- How many hazards can lead to this consequence?

Reading the bowtie diagram from left to right, one can imagine incident scenarios by stepping through the diagram elements. For example, once a threat is identified, one can progress to the barriers that prevent or intervene that threat, which would eliminate the probability of the top event being triggered. If those barriers are broken, however, this may be the result of outside escalation factors or equipment failures. Once the top event is triggered, the timeline is now shifted to the right side of the diagram. Barriers along the path to the consequence will hopefully prevent the consequence from being fully realized. The general structure of bowtie model is illustrated in Figure 19.

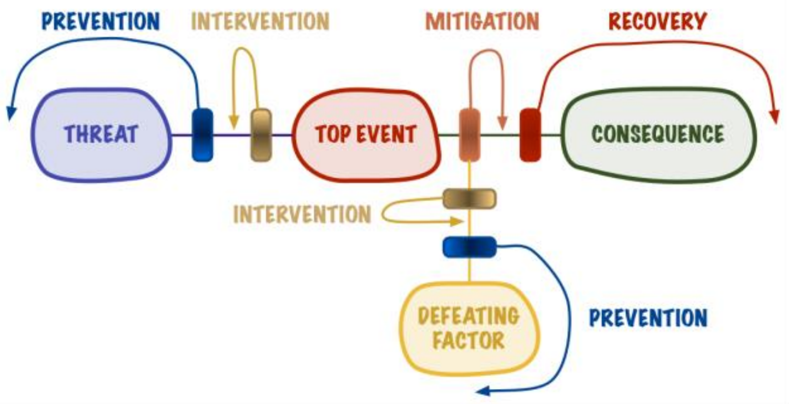


Figure 19 Generalized Bowtie model structure.

The Bowtie model permits the addition of qualitative severity and probability rankings. This is obtained by building a risk-consequence matrix with qualitative axes related to the context of the analysis. The categories in the risk-consequence matrix are numbered on the vertical axis (severity) and lettered on the horizontal axis (frequency). Thus the risk ranking is a coordinate system label such as "A1" or "B4". The higher the letter and number, the higher the risk. This is shown in a simpler form in Figure 20.

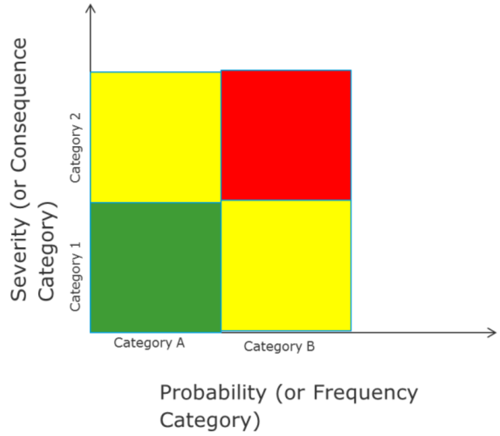


Figure 20 Generalized risk categories

9.15 Determination of Risk

Within the Bowtie structure there are "buttons" on the consequences and the top event that are labled "B3" or "A2", etc. In general, when reading risk charts, the following relationship should be remembered:

$$Risk = Probability * Consequence$$

The charts below are qualitative risk rankings based on this mathematical relationship. They are based on a qualitative assignment of relative consequence and the frequency of the occurrence in the company (client's company) or its industry or related industries[11]. Below is Bowtie XP's output and description of the "buttons" on the consequence element of the model. The charts should be read in the following fashion:

- The vertical column on the left is a qualitative consequence category (0,1,2,3…)
- The horizontal row along the top is a qualitative probability category (A, B, C, …)
- The numbers in each are a relative risk (A1, B3,…) rankings based on the qualitative relevance to this project

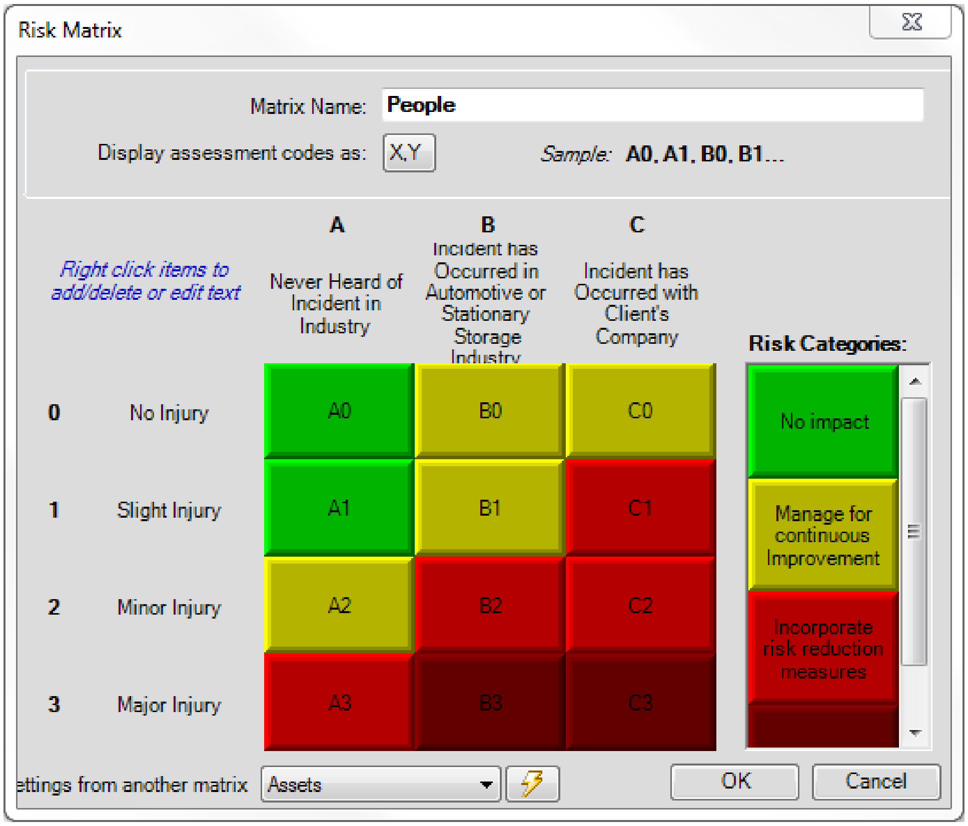
There are four general risk categories listed under the top event and consequences, represented by four "buttons" from left to right: ***People***, ***Asset***, ***Environment***, and ***Reputation***.

---

[11] Inherent Risk is risk that an activity would pose if no controls were in place. Residual Risk is risk that remains after controls are in place. Bowtie XP indicates inherent risk with brackets "[]" around the value.

Example: in the "people" category, a loss of battery control has been seen before in the automotive energy storage industry and no injuries were reported. Examples include: the Tesla battery fire from collision with road debris, or the Xtreme Power battery fire in Hawaii. More recently, incidents with Boeing may influence this category. An example where an injury has been reported is the explosion in the GM battery test lab that injured GM employees. Qualitatively including these incidents in the "people" matrix and categorizing them in the "Incident has Occurred in Automotive or Stationary Storage Industry" helps provide context around the relevance, probability, and possible consequence of this risk.

Bowtie XP accounts for inputs using the risk ranking box shown in Figure 21. The user clicks on the box based on knowledge about the industry and related events*. In this manner, lessons learned from the industry are translated directly to client's company.*



Matrix Name: **People**

Display assessment codes as: X,Y

Sample: **A0, A1, B0, B1...**

Right click items to add/delete or edit text

		A Never Heard of Incident in Industry	**B** Incident has Occurred in Automotive or Stationary Storage Industry	**C** Incident has Occurred with Client's Company
0	No Injury	🟩 A0	🟨 B0	🟨 C0
1	Slight Injury	🟩 A1	🟨 B1	🟥 C1
2	Minor Injury	🟨 A2	🟥 B2	🟥 C2
3	Major Injury	🟥 A3	🟫 B3	🟫 C3

Risk Categories:

- 🟩 No impact
- 🟨 Manage for continuous Improvement
- 🟥 Incorporate risk reduction measures
- 🟫

Figure 21 Example Risk Matrix from Bowtie XP – "people" category.

ABOUT DNV GL

Driven by our purpose of safeguarding life, property and the environment, DNV GL enables organizations to advance the safety and sustainability of their business. We provide classification and technical assurance along with software and independent expert advisory services to the maritime, oil and gas, and energy industries. We also provide certification services to customers across a wide range of industries. Operating in more than 100 countries, our 16,000 professionals are dedicated to helping our customers make the world safer, smarter and greener.