

EVS-GTR

Electrolyte leakage



| Test items | Present Requirements | |
|---|--|--|
| Vibration | -No evidence of electrolyte leakage | |
| Thermal shock and cycling | -The evidence of electrolyte leakage shall be verified by visual inspection without disassembling any part of the Tested-Device | |
| External short circuit protection | | |
| Overcharge protection | | |
| Over-discharge protection | | |
| Over-temperature protection | | |
| Mechanical shock | -No evidence of electrolyte leakage | |
| Mechanical integrity | -The evidence of electrolyte leakage shall be verified by visual inspection without disassembling any part of the Tested-Device -An appropriate coating shall, if necessary, be applied to the physical protection (casing) in order to confirm if there is any electrolyte leakage from the REESS resulting from the test. Unless the manufacturer provides a means to differentiate between the leakage of different liquids, all liquid leakage shall be considered as the electrolyte. | |
| REESS requirements for whole vehicle post-crash | -For a period from the impact until 30 minutes after the impact, there shall be no electrolyte leakage from the REESS into the passenger compartment -and no more than 7 per cent by volume of the REESS electrolyte capacity spilled from the REESS to the outside of the passenger compartment . | |



50

40

30

20

10

Object

vehicle

Opponent

vehicle

truck

v.s. Heavy truck

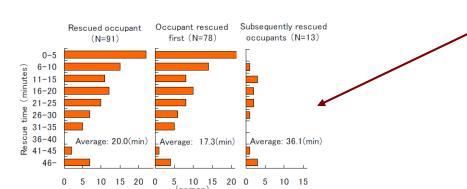
Study from Japan Automotive Research Institute (JARI) and Japan Automotive Manufacturers Association (JAMA)*:

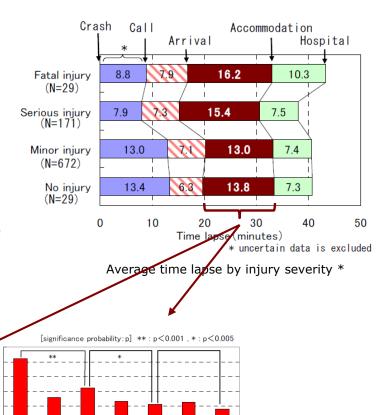
- Various crash scenarios are considered among passenger cars as well as involving heavier vehicles (trucks)
- Statistical analysis of the 1996-2006 field data in Japan shows that:

 the <u>average</u> "Crash" – "Accommodation" time often significantly exceeds 30 minutes

 especially when more than 1 occupant is to be rescued

- and/or when a truck is involved





* Y.Sukegawa, M.Sekino, "Analysis of rescue operations of injured vehicle occupants by fire fighters", paper#11-0101, presented at the 22nd Enhanced Safety of Vehicles Conference (ESV-22), Washington DC, June 2011. www.nrd.nhtsa.dot.gov/departments/esv/22nd/

v.s. Passenger car

v.s. Structure

around road



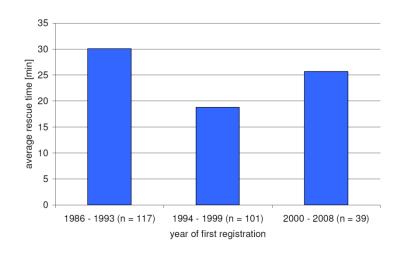
To our knowledge little data is available for Europe.

Rescue approach varies **:

- "Scoop and run" transport a victim ASAP to a hospital US
- "Stay and play" stabilise the patient at the scene Germany

Results of the German study** show that:

- the average rescue time ("Arrival" to "Accommodation") often exceeds 25 min;
- rescue time does not solely depend on technical issues as a medical treatment to stabilise the patient often occurs in parallel;
- rescue time may depend on the model, i.e. increase for newer cars.



^{* *} H. Johannsen, G. Muller, C. Pastor, R-D. Erbe, H-G. Schlosser, "Influence of new car body design on emergency rescue", paper presented at the 4th International Conference on ESAR "Expert Symposium on Accident Research", Hannover, September 2010; http://bast.opus.hbz-nrw.de/volltexte/2012/556/



USA data analysis***:

- The available sources of quantified information are limited
- Disaggregation of urban and rural data for response time analysis is consistently identified
- Average "Crash" to "Call" time varies between 4 and 7 to 8 min
- Average "Call" to "Arrival" time varies between 4 and 11 min
- No data available in this study on "Arrival" to "Accommodation" time

Table 2 Summary of Published Response Time Values

| Table 2 Summary of Published Response Time Values | | | | | |
|---|-------------|---------------|-------------------------|---|--|
| Interval | Time | Average or | Data Description | Source | |
| | (Minutes) | Percentage of | | | |
| | | Calls | | | |
| | • 0.5 | Included | 771 4004 5 1 5 1 5 1 5 | ed : • | |
| | 3.87 | Average | Urban, 1996 Fatal, EMS | Champion, 3- | |
| | 7.36 | Ü | Rural, 1996 Fatal, EMS | 4/1999 | |
| Crash to | 4 | Average | Urban, 1997 Fatal, EMS | Champion, 5/1999 ¹ | |
| Notification | 7 | | Rural, 1997 Fatal, EMS | - | |
| | 8.4 minutes | | Urban | Mayor's Committee | |
| | 3.9 minutes | Average | Urban, Adjusted | for Urban Renewal, | |
| | | | | 1970 | |
| | 4:19 | Average, US | | | |
| | | cities | First Unit | Phoenix Survey, | |
| | 4:30 | 80%, US | That Chit | 2000^2 | |
| | | cities | | | |
| | 0-10 | 81.7% | Rural Fatal, EMS | | |
| | 0-20 | 94.3% | Rural Fatal, EMS | Traffic Safety Facts, 2001 ³ | |
| | 0-10 | 93.8% | Urban Fatal, EMS | | |
| | 0-20 | 97.7% | Urban Fatal, EMS | | |
| | 6 | Average | Urban, 1997, Fatal, EMS | Champion, 5/1999 ¹ | |
| | 11 | Average | Rural, 1997 Fatal, EMS | Champion, 5/1999 | |
| | 0-10 | 88.3% | Urban, 1975-1993 Fatal, | | |
| | | | EMS | | |
| Notification | 0-10 | 57.7% | Rural, 1975-1993 Fatal, | | |
| to Arrival | | | EMS | Tessmer, 1996 ⁴ | |
| | 0-20 | 97.8% | Urban, 1975-1993 Fatal, | ressilier, 1990 | |
| | | | EMS | | |
| | 0-20 | 89% | Rural, 1975-1993 Fatal, | | |
| | | | EMS | | |
| | 5.1 | | 2000, Fire Service | | |
| | 5.3 | Arraraga | 2001, Fire Service | | |
| | 5.4 | Average | 2002, Fire Service | | |
| | 5.3 | | 2003, Fire Service | CA NFIRS ⁵ | |
| | | 80% | 2000, Fire Service | CANTINO | |
| | 0-7 | 77% | 2001, Fire Service | | |
| | U- / | 75% | 2002, Fire Service | | |
| | | 77% | 2003, Fire Service | | |

^{***} L.E. Shields, "Emergency Response Time in Motor Vehicle Crashes: Literature and Resource Search", report prepared for Motor Vehicle Fire Research Institute, January 2004. http://www.mvfri.org/Contracts/Final%20Reports/Shields Report-01.pdf



Summary:

- 1) "Crash" to "Accommodation" time needs to be considered. This includes: "Crash" to "Call", "Call" to "Arrival" and "Arrival" to "Accommodation" time slots.
- 2) "Crash" to "Accommodation" time depends on many parameters such as:
- a) density of population, rural/urban area
- b) type of an accident, including car model, number of occupants, involvement of heavier vehicles
- c) availability of the rescue workers (fire fighters, ambulance)
- d) ...

and may, therefore, vary from country to country;

3) Rescue equipment and approach are different in different countries, making statistical data not directly relevant to other areas



We propose:

- To increase the "no leak" time slot to at least 60 minutes.

| Area/ average time, min | Crash-Call | Call-Arrival | Arrival-Accommodation | Total |
|----------------------------|------------|--------------|-----------------------|-----------|
| Japan* | 13 | 8 | up to 36 | up to 57 |
| China | | | | |
| South Korea | | | | |
| USA***, Canada | 4 to 8 | 4 to 11 | | > 8 to 19 |
| Europe | | 8 (NL) | 25** (DE) | > 33 |

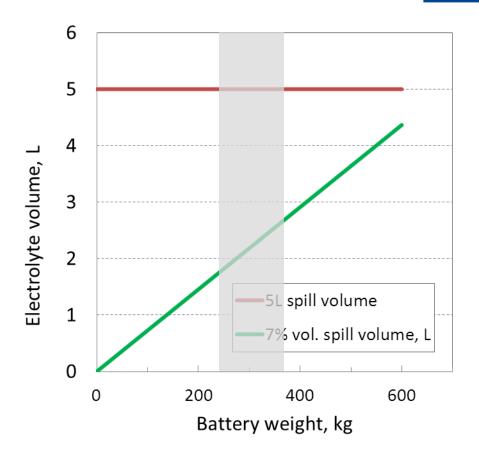
More data for various regions needs to be collected to better define the "no leak" time slot for the present EVS-GTR

^{*} Y.Sukegawa, M.Sekino, "Analysis of rescue operations of injured vehicle occupants by fire fighters", paper#11-0101, presented at the 22nd Enhanced Safety of Vehicles Conference (ESV-22), Washington DC, June 2011. www.nrd.nhtsa.dot.gov/departments/esv/22nd/

^{**} H. Johannsen, G. Muller, C. Pastor, R-D. Erbe, H-G. Schlosser, "Influence of new car body design on emergency rescue", paper presented at the 4th International Conference on ESAR "Expert Symposium on Accident Research", Hannover, September 2010; http://bast.opus.hbz-nrw.de/volltexte/2012/556/

^{***} L.E. Shields, "Emergency Response Time in Motor Vehicle Crashes: Literature and Resource Search", report prepared for Motor Vehicle Fire Research Institute, January 2004. http://www.mvfri.org/Contracts/Final%20Reports/Shields Report-01.pdf





Assuming 13 wt% electrolyte content in a battery

 7 vol% is a more stringent requirement than 5 L spill for most of the Li-ion battery sizes

Spilling ca. 1 L of dimethyl carbonate results in a PAC-3 concentration level in a volume of vehicle +3 m-thick layer around it

PAC stands for Protective Action Criteria

PAC-1: Mild, transient health effect

PAC-2: Irreversible or other serious health effects that could impair the ability to take protective action

PAC-3: Life-threatening health effects



Li-ion solvents

We considered the following conventional electrolyte solvents:

- 1) Ethyl acetate (EA), CAS # 141-78-6;
- 2) Dimethyl carbonate (DMC), CAS # 616-38-6
- 3) Ethyl methyl carbonate (EMC), CAS # 623-53-0
- 4) Diethyl carbonate (DEC), CAS # 105-58-8
- 5) Propylene carbonate (PC), CAS # 108-32-7
- 6) Ethylene carbonate (EC), CAS # 96-49-1
- 7) Tetrahydrofuran (THF), CAS # 109-99-9
- 8) Acetonitrile (AN), CAS # 75-05-8 (also used in supercapacitors)
- 9) γ -Butyrolactone (γ -BL), CAS # 96-48-0
- 10) 1,2-Dimethoxyethane (DME), CAS # 110-71-4
- 11) 1,3-Dioxolane, CAS # 646-06-0



Li-ion solvents

| Solvent | Volume of evaporated solvent*, cm³ | | |
|--|------------------------------------|-------------|--|
| | PAC-2 level | PAC-3 level | |
| γ-Butyrolactone (γ-BL), CAS # 96-48-0 | 0.22 | 17 | |
| Dimethyl carbonate (DMC), CAS # 616-38-6 | 25 | 149 | |
| Tetrahydrofuran (THF), CAS # 109-99-9 | 104 | 1038 | |

^{*} Volume, solvent evaporates into, is defined as vehicle + 1-m-thick layer around it; 61.5 m³ in this study

Small spills – 0.2 to 150 cm³ - lead to dangerous situations Small amount needs to be measured – impact on the method choice



Li-ion salts

| Lithium Hexafluorophosphate | LiPF ₆ |
|-----------------------------|-------------------|
| Lithium Hexafluorophosphate | LiPF |

Lithium Tetrafluoroborate LiBF₄

Lithium Hexafluoroarsenate LiAsF₆

Lithium Iodide LiI

Lithium Perchlorate LiClO₄

Lithium Trifluoromethane Sulfonate LiCF₃SO₃

Lithium Bis (Trifluromethanesulfonyl) Imide LiN(CF₃SO₂)₂

Lithium Bis(Perfluoroethylsulfonyl) Imide LiN(CF₃CF₂SO₂)₂

Lithium Bis(Oxalato)Borate LiB(C₂O₄)₂

Tetraethyl-Ammonium Tetrafluoroborate (C₂H₅)₄NBF₄

Triethyl-Methyl-Ammonium Tetrafluoroborate $(C_2H_5)_3CH_3NBF_4$

Some decomposition products of the salts, e.g. HF, may further limit the maximum allowed electrolyte leakage...

work in progress

Outside vs. Inside



How relevant is the distinction between "outside" the passenger compartment from "inside" the compartment after a crash and/or during the rescue operation?

One of the phases in the rescue operation is removal of the windows.

Proposal



We propose:

- Differentiation of the maximum allowed electrolyte leakage per REESS type (e.g. aqueous vs. non-aqueous electrolyte based) may be a good approach;
- Change text for Li-ion based REESS as follows:

REESS requirements for whole vehicle post-crash

-For a period from the impact until 30 minutes after the impact, there shall be no electrolyte leakage from the REESS into the passenger compartment

-and no more than 7 per cent by volume of the REESS electrolyte capacity spilled from the REESS to the outside of the passenger compartment.



REESS requirements for whole vehicle post-crash

For a period from the impact until 60 minutes after the impact, there shall be no more than X ml electrolyte leakage from the REESS

Can the amounts acceptable from the toxicology point be reliably measured in a full vehicle crash test?

How to measure?



Weight loss measurement is unlikely to be reliable: 0.5 to 300 cm³, i.e. grams on the scale of a full vehicle / REESS

Is it possible to measure such a small weight loss? Also considering that components will be volatile.

<u>Visual inspection</u> may be difficult due to toxic and volatile electrolyte components in case of Li-ion based REESS

Is gas analysis (quantification) required? Should requirement be based on the gas concentration and not volume/mass leaked?

Is this possible with range of potential electrolyte components?

<u>Analytical techniques</u> such as gas chromatography (GC), infrared spectroscopy (FTIR), mass spectrometry (MS) etc. may be required to:

- a) Quantify the electrolyte leakage,
- b) Differentiate between electrolyte leakage and combustion.