# New Zinc-Based Automotive Steel Protection Technologies

## ZCO-45-6

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# Objectives

- **To investigate corrosion properties of binary Zn-X, ternary Zn-Mg-X, Zn-Al-X,** and **quaternary Zn-Al-Mg-X cast alloys** in order to identify compositions for future hot-dip materials for automotive industry

# Outline: Three stages

- **Stage A: Screening**. Prepare 30–40 binary and ternary alloys. Characterize their corrosion stability and ability to provide galvanic protection. *2011–2012.* ***Finished.***
- **Stage B: Tailoring of alloy properties**. Based on results of Stage A, prepare and characterize about 20 additional alloys with adjusted composition/structure. *2012–2013.* ***Finished.***
- **Stage C: Protection in confined zones and mechanism**. Hem flange protection often critical for automotive applications. 11 new materials. *2013–2014.* ***In progress.***

# Stage A+B: Alloy selection



- **A**: Main focus on **ternary alloys with Mg / Al** with concentration of X up to 2 wt. %
  - **Zn-5Al-X:** Galfan-based
  - **Zn-6Mg-X:** $Mg_2Zn_{11}$ phase shows best stability
  - Binary **Zn-X**: Reference
- **B**: Quaternary **Zn-3Al-2Mg-X** alloys, because of:
  - Limited potential for improvement of corrosion stability for ternary alloys in comparison to Zn-Mg and Zn-Al
  - Better fabrication properties
- 58 compositions prepared in total

# Stage A+B: Prepared alloys

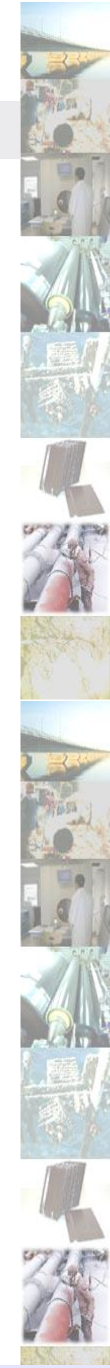


| Material | Chemical comp. [wt. %] | | | |
|---|---|---|---|---|
| | Zn | Mg | Al | X |
| Zn | 100 | | | |
| Zn-2Ti | 97.3 | | | 1.7 |
| Zn-2Mm | 96.8 | | | 1.9 |
| Zn-2Zr | 97.5 | | | 1.8 |
| Zn-0.01Mo | 99.5 | | | 0.01 |
| Zn-0.6Cr | 99.0 | | | 0.6 |
| Zn-0.0003B | 99.3 | | | 0.0003 |
| Zn-2Ga | 97.5 | | | 1.8 |
| Zn-2In | 97.7 | | | 1.8 |
| Zn-2Cu | 98.0 | | | 1.7 |
| Zn-2Ni | 97.1 | | | 2.5 |
| Zn-0.01Si | 100.0 | | | <0.01 |
| Zn-1Ca | 98.0 | | | 1.5 |
| Zn-2Mg | 97.8 | | | 2.0 |
| Zn-7Mg | 93.0 | | | 6.8 |
| Zn-2Al | 97.8 | | | 2.1 |
| Zn-3Al | 96.6 | | | 3.1 |
| Zn-5Al | 94.7 | | | 5.2 |
| Zn-2Mg-0.6Cr | 97.5 | 2.0 | | 0.6 |
| Zn-7Mg-1Ti | 92.4 | 6.8 | | 0.6 |
| Zn-7Mg-1Mm | 91.2 | 7.2 | | 1.2 |
| Zn-7Mg-2Zr | 90.5 | 7.5 | | 1.8 |
| Zn-7Mg-0.01Mo | 93.0 | 6.7 | | 0.01 |
| Zn-7Mg-0.5Cr | 92.9 | 6.6 | | 0.5 |
| Zn-7Mg-0.004B | 92.0 | 7.3 | | 0.004 |
| Zn-10Mg-2Ga | 87.3 | 10.4 | | 2.0 |
| Zn-6Mg-2In | 92.1 | 6.1 | | 1.8 |
| Zn-7Mg-2Cu | 90.9 | 6.8 | | 2.1 |
| Zn-7Mg-2Ni | 91.1 | 6.5 | | 2.2 |
| Zn-7Mg-1Ca | 92.2 | 6.5 | | 1.1 |

| Material | Chemical comp. [wt. %] | | | |
|---|---|---|---|---|
| | Zn | Mg | Al | X |
| Zn-3Al-0.6Cr | 96.4 | | 3.0 | 0.6 |
| Zn-8Al-2Ti | 89.4 | | 8.3 | 2.0 |
| Zn-9Al-2Mm | 89.0 | | 8.6 | 1.6 |
| Zn-7Al-1Zr | 92.0 | | 6.7 | 1.1 |
| Zn-8Al-0.01Mo | 92.1 | | 7.6 | 0.01 |
| Zn-6Al-0.4Cr | 93.0 | | 6.3 | 0.4 |
| Zn-6Al-0.0003B | 93.3 | | 6.0 | 0.0003 |
| Zn-6Al-2Ga | 92.1 | | 5.8 | 2.0 |
| Zn-6Al-2In | 92.1 | | 5.6 | 1.9 |
| Zn-6Al-2Cu | 91.8 | | 6.3 | 1.6 |
| Zn-8Al-2Ni | 89.9 | | 7.7 | 2.0 |
| Zn-6Al-1Ca | 92.4 | | 5.7 | 1.4 |
| Zn-3Al-2Mg | 94.9 | 2.1 | 3.0 | |
| Zn-3Al-2Mg-0.2Cr | 94.6 | 2.1 | 3.1 | 0.2 |
| Zn-3Al-2Mg-0.5Cr | 94.8 | 2.0 | 3.1 | 0.5 |
| Zn-3Al-2Mg-0.2Zr | 94.7 | 2.1 | 3.0 | 0.2 |
| Zn-3Al-2Mg-0.6Zr | 94.3 | 2.0 | 3.1 | 0.6 |
| Zn-3Al-2Mg-2Zr | 93.2 | 2.0 | 2.9 | 2.0 |
| Zn-3Al-2Mg-0.2Ti | 94.6 | 2.0 | 3.1 | 0.2 |
| Zn-3Al-2Mg-0.6Ti | 94.3 | 2.0 | 3.1 | 0.6 |
| Zn-3Al-2Mg-2Ti | 92.6 | 2.1 | 3.1 | 2.1 |
| Zn-3Al-3Mg-0.3Mm | 93.6 | 3.1 | 3.0 | 0.3 |
| Zn-3Al-2Mg-0.6Mm | 94.1 | 2.1 | 3.1 | 0.6 |
| Zn-3Al-2Mg-0.01Mo | 94.8 | 2.1 | 3.1 | 0.01 |
| Zn-3Al-2Mg-0.2Mn | 94.8 | 2.1 | 2.9 | 0.2 |
| Zn-3Al-2Mg-0.6Mn | 94.2 | 2.1 | 3.1 | 0.6 |
| Zn-3Al-2Mg-2Mn | 92.8 | 2.1 | 3.1 | 1.9 |
| Zn-3Al-2Mg-2Si | 93.1 | 2.0 | 3.0 | 1.9 |

*Mm: Mischmetal, mixture of lanthanides (typically 51% Ce, 26% La, 17% Nd, 6% Pr)*

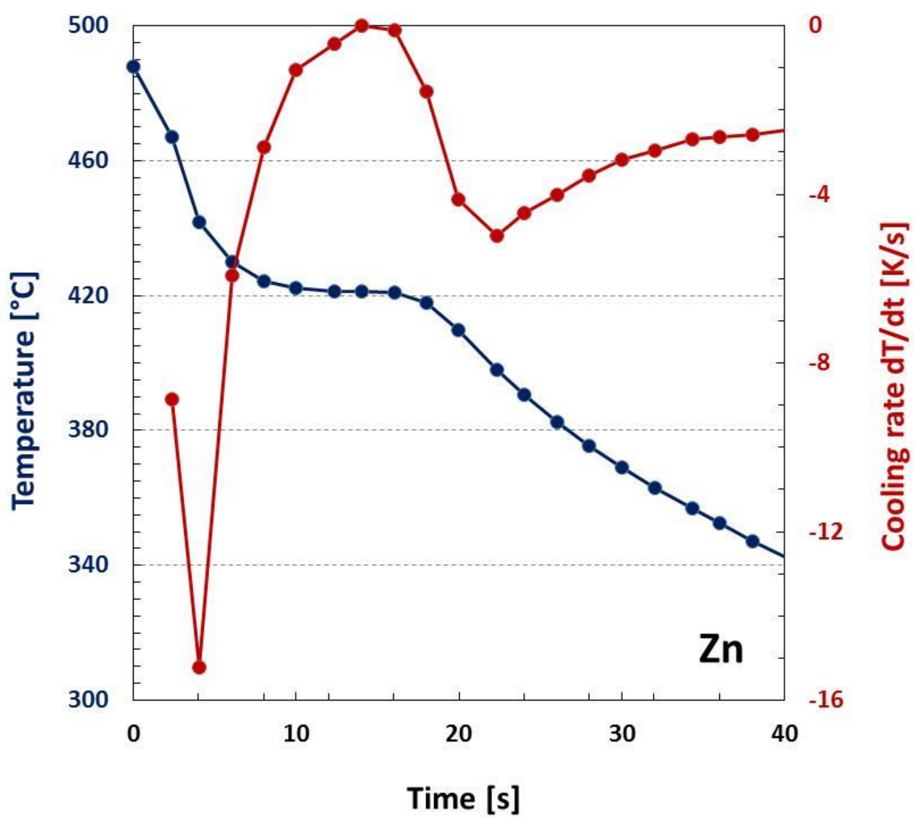
*Alloys in red require use of protective atmosphere due to formation of excess of dross*



# Stage A+B: Preparation



- **Induction melting** in graphite crucible under Ar
- Purity 99% or better (Zn, Mg: Purity 99.99%)
- **Casting** at 500-800 °C under argon into a brass mold, rods of Ø50 mm
- **Cooling rate**: About 3 K/s →
- **Homogenization annealing** (only A)
- **Cutting** to round samples, thickness 2–3 mm
- **Polishing** to grit 400



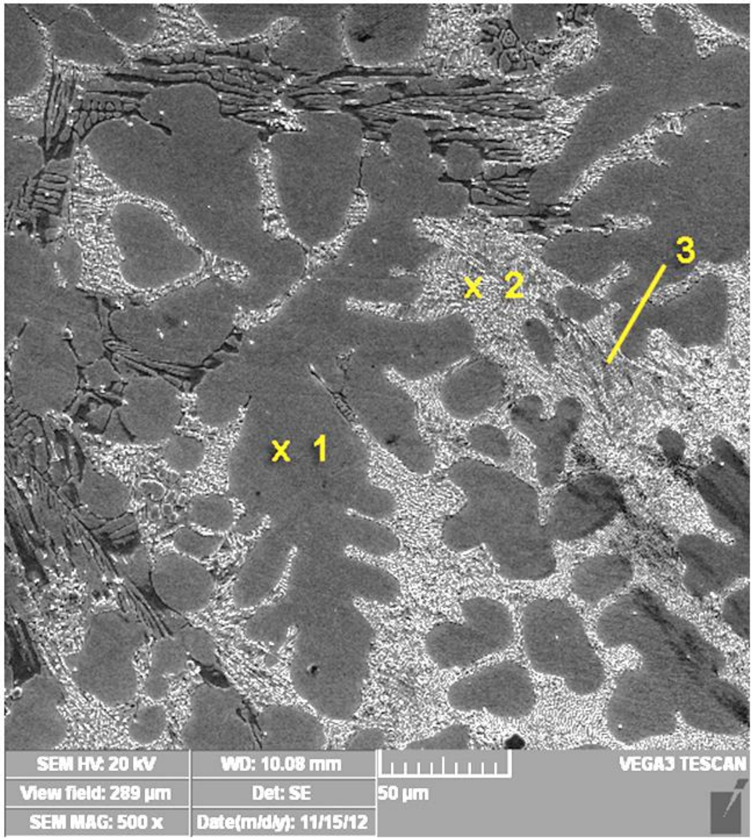
# Stage A+B: Characterization

- **Chemical analysis** by x-ray fluorescence (XRF)
- **Phase analysis** by x-ray diffraction (XRD)
- **Microstructure characterization** by light and electron microscopy (SEM)
- **Hardness measurement**
- **DSC analysis**

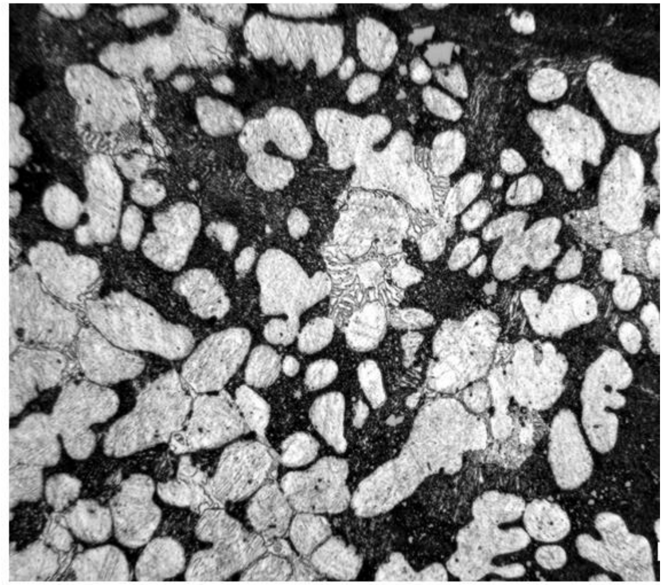

*Wet abrasive cutter*


*SEM*

# Example: Zn-3Al-2Mg-0.2Cr




Microstructure (SEM)



**Microstructure of alloy** (Light microscope)

## Hardness

118 HV 5

## Preparation of alloy

**Casting:**
melting 750°C / 6h
**Heat treatment:**
none

## Notes

## Chemical composition [wt.%]

| Al | Mg | Cr |
|---|---|---|
| 3.11 | 2.08 | 0.21 |

## Description of the microstructure

Primary dendrites of ZnAlMg solid solution (1); ZnAl + $Mg_2Zn_{11}$ eutectic (2); AlCr phases (3)

## Phases detected by XRD

ZnAl solid solution; $Mg_2Zn_{11}$

## Phases detected by SEM

ZnAl solid solution; $Mg_2Zn_{11}$; particles of AlCr phases

## Expected phases

ZnAl solid solution; $Mg_2Zn_{11}$; $Zn_{17}Cr$; $Al_7Cr$

# Stage B: Solidification

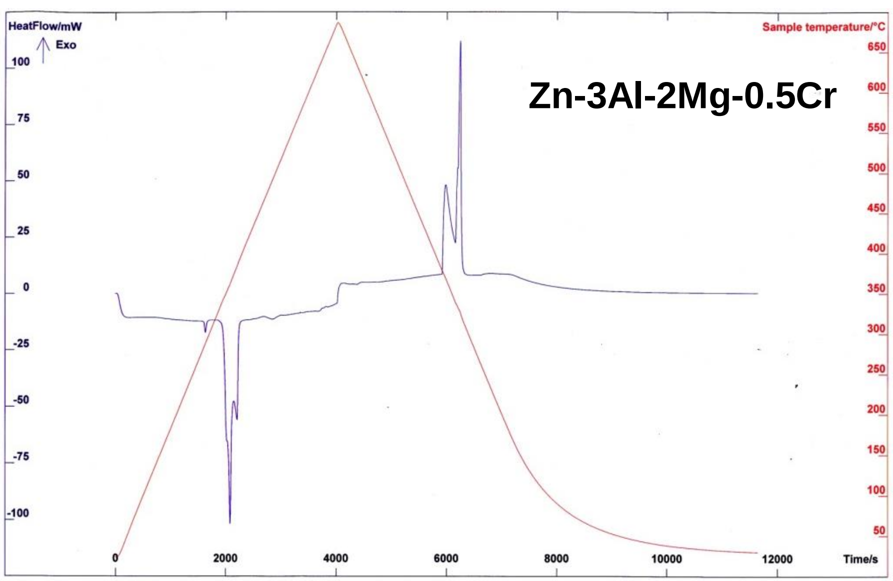


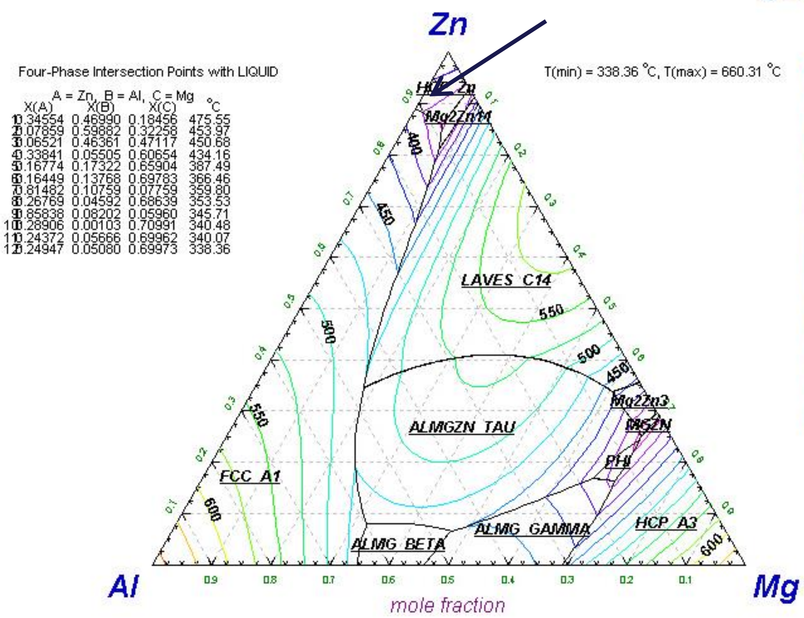
- DSC measurement, 25 → 700 → 25 °C, 10 K/min

**Temperature intervals of crystallization [°C]**

| Alloy | Heating | | Cooling | |
|---|---|---|---|---|
| | Solidus | Liquidus | Liquidus | Solidus |
| Zn-3Al-2Mg | 345 | 390 | 375 | 300 |
| Zn-3Al-2Mg-2Si | 350 | 395 | 350 | 305 |
| Zn-3Al-2Mg-0.6Mm | 345 | 390 | 360 | 295 |
| Zn-3Al-2Mg-0.5Cr | 335 | 395 | 375 | 310 |

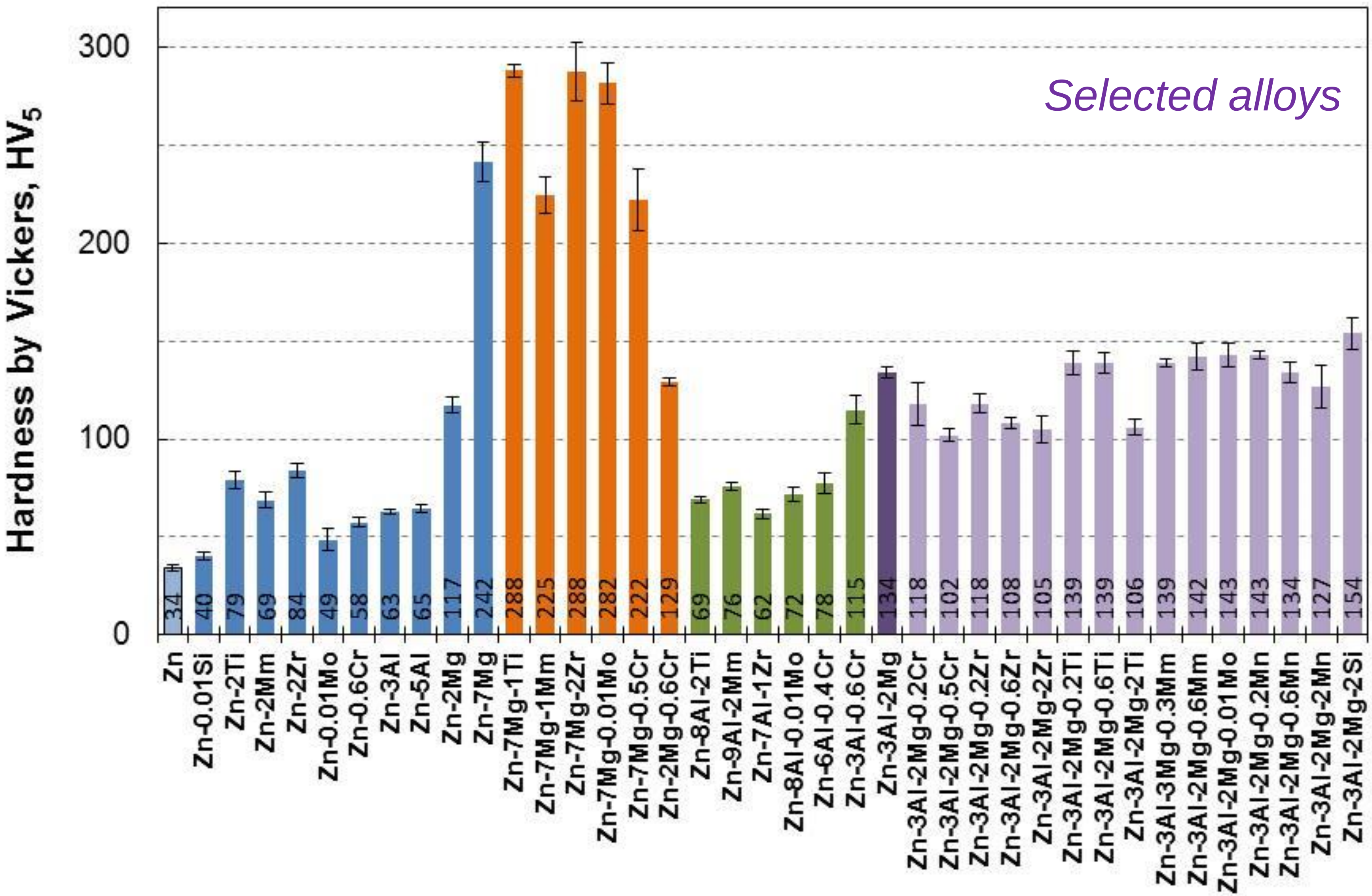
**Decrease compared to zinc**




# Stage A+B: Hardness





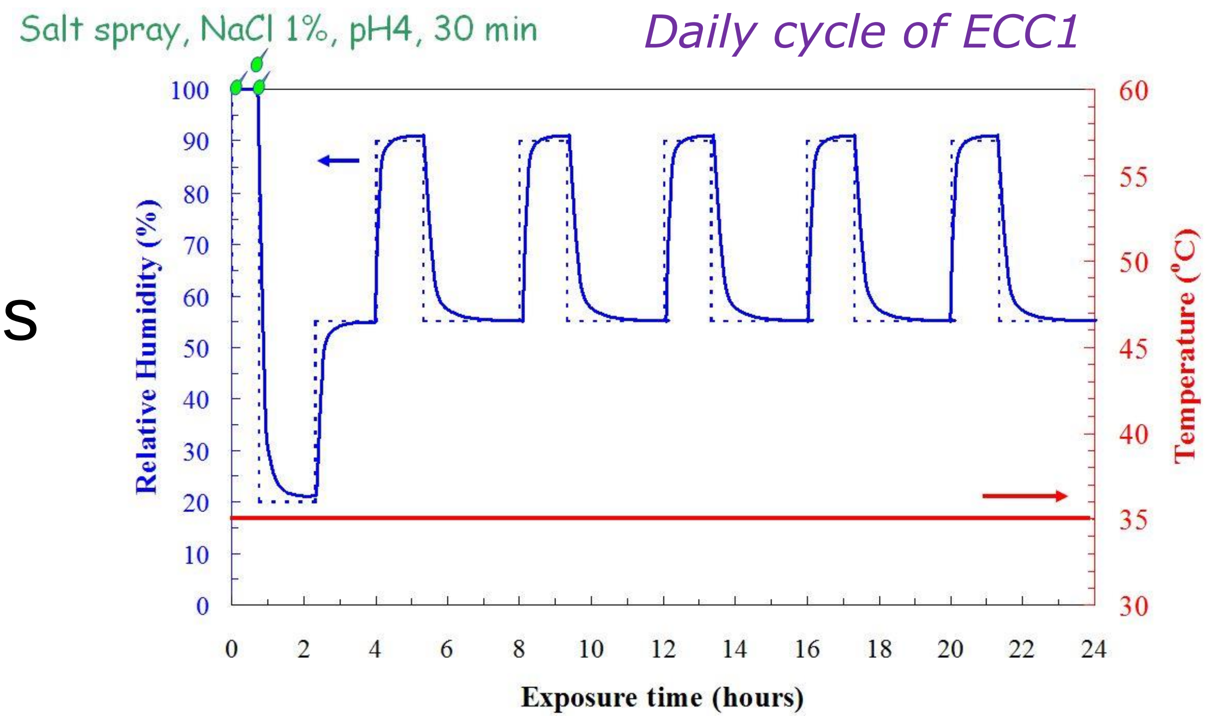
# Stage A+B: Corrosion

- **Mass loss measurements**:
  - Cyclic accelerated test used for automotive materials, Renault **ECC1** D17 2028
  - **Static** test under chloride/sulphate deposits
  - Outdoor **field exposure**
- **Corrosion spreading**: Surface activity
- **Galvanic protection of steel**: Electrochemical measurements in water, red rust protection in water and in ECC1
- *Reference hot-dip materials: HDG, Zn-5Al (Galfan), Zn-55Al (AZ150), Zn-1.5Al-1.5Mg (Zn2Al2Mg), Zn-2.4Al-2.8Mg (Zn2Al3Mg), Zn-11Al-3Mg (SD)*

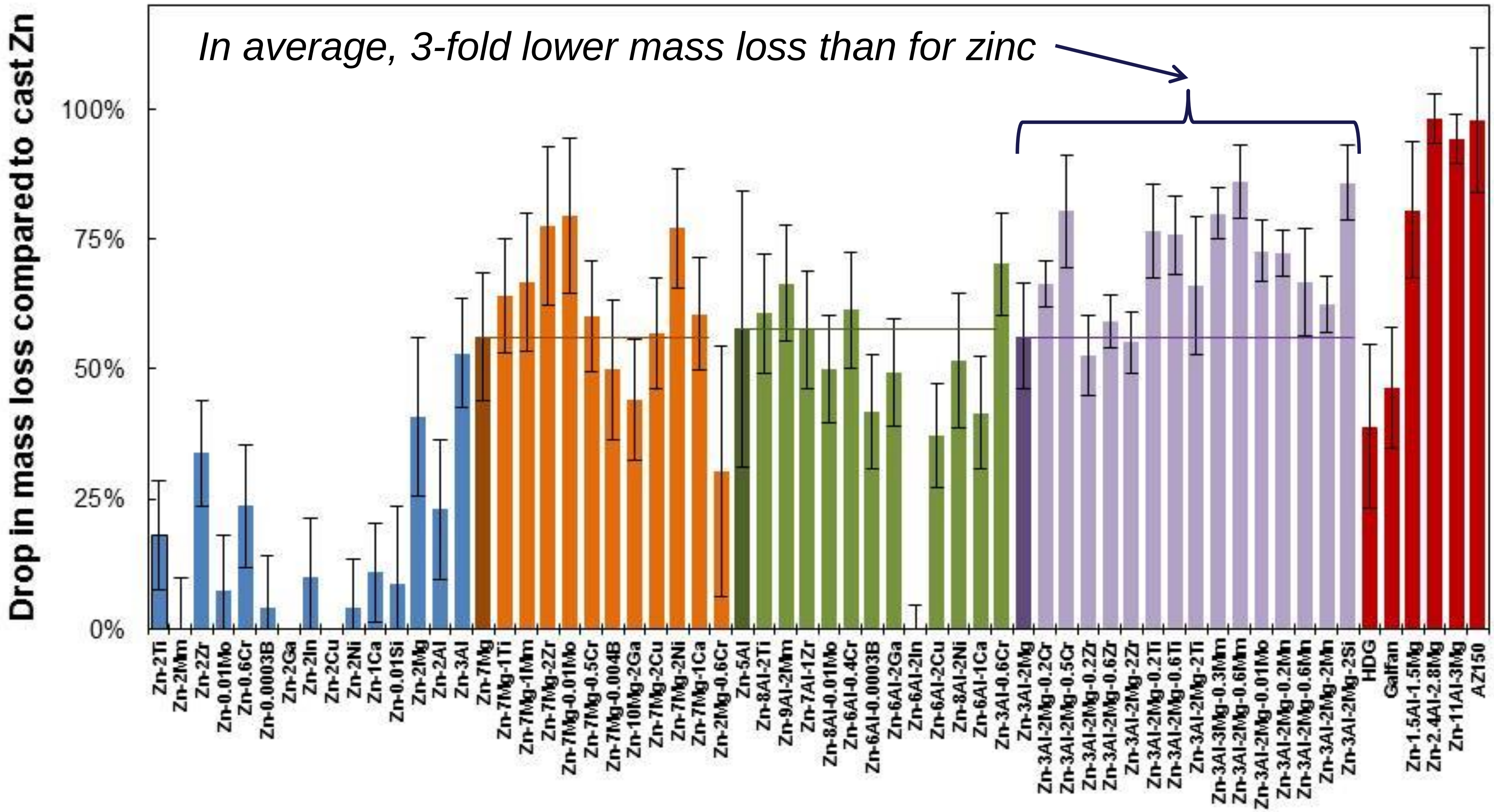
# Stage A+B: ECC1



- ECC1 test by Renault (D17 2028 standard)
- NaCl spray once a day
- 35 °C
- Wet/dry cycles
- 6 weeks
- 3–4 parallel samples, masked with tape on back
- Pickling according to ISO 8407 in glycine



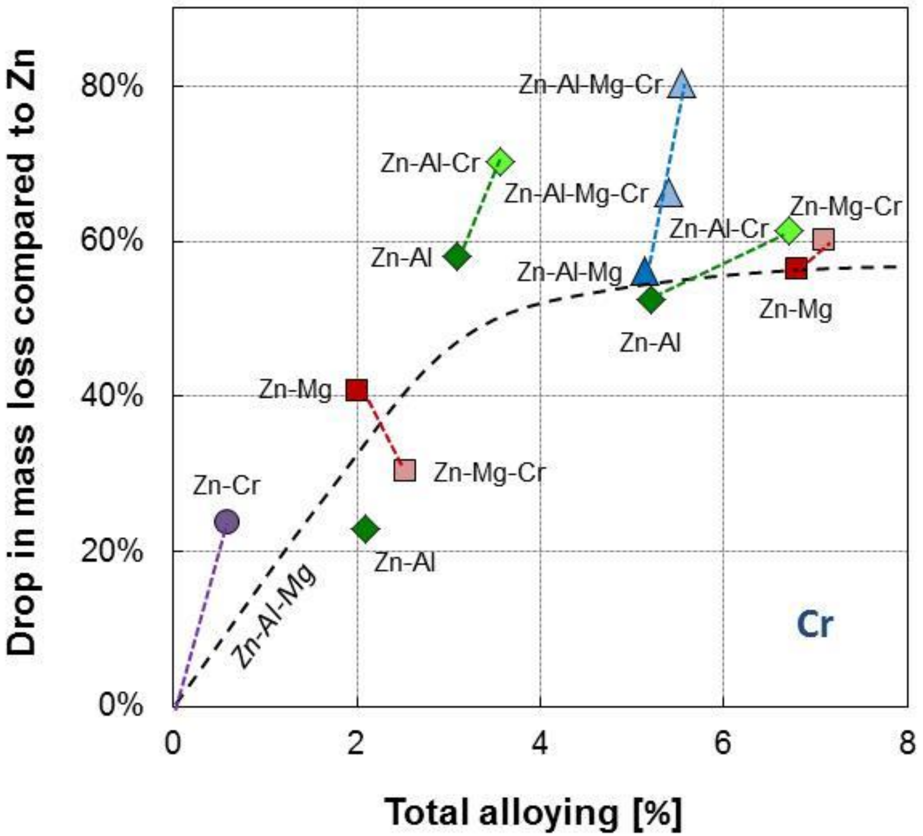

# Stage A+B: ECC1

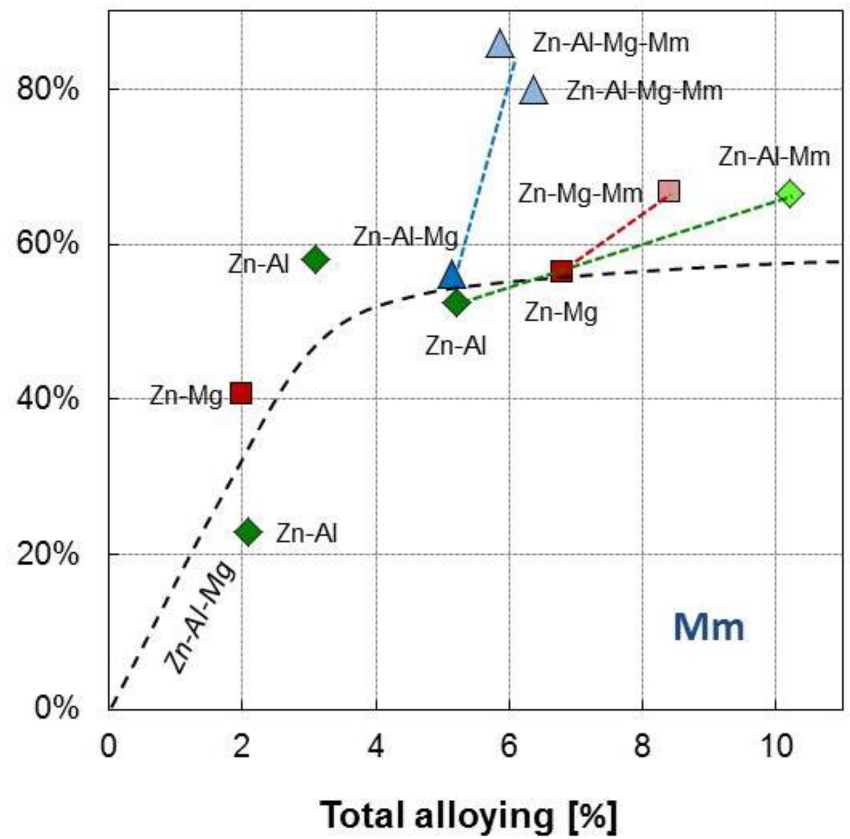



**Zn-X:** Only Mg and Al efficient; **Zn-5Al-X:** Minor improvements compared to Zn-5Al; **Zn-7Mg-X, Zn-3Al-2Mg-X**: Several materials promising

# Stage A+B: ECC1






- **Cr**: Small effect in Zn-Mg
- Stronger effect in Zn-Al
- Significant improvement for Zn-3Al-2Mg (**+0.5% Cr**: 2-fold lower mass loss; compared to Zn 5-fold)

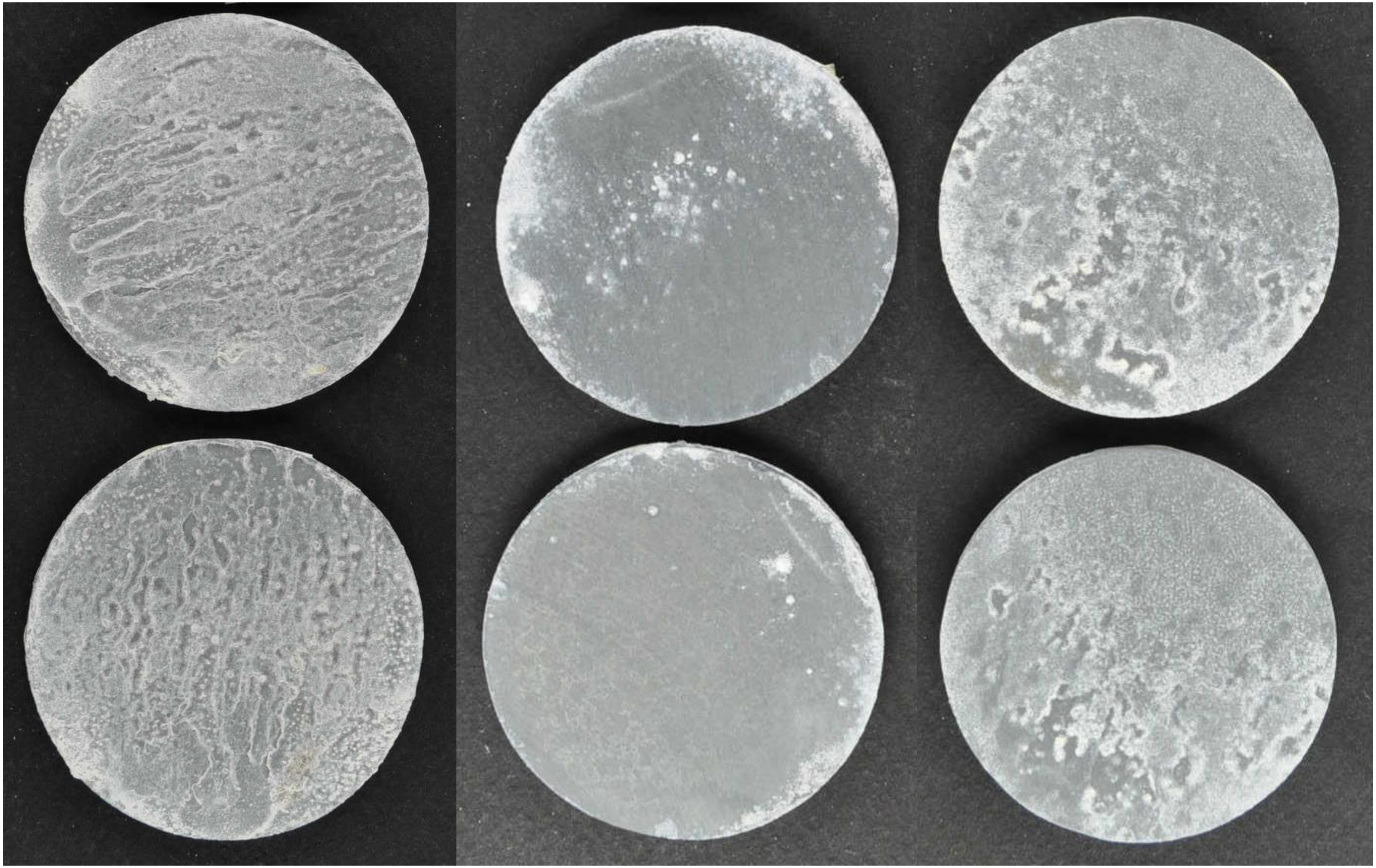
- **Mm (Ce)** improved stability of all alloys except for pure Zn
- **+0.6% Mm**: 3-fold lower mass loss compared to Zn-3Al-2Mg (7-fold compared to Zn)

# Stage A+B: ECC1

- **Si**: Very good results for **Zn-3Al-2Mg-2Si**: 3-fold lower mass loss compared to Zn-3Al-2Mg and 7-fold lower compared to Zn
- **Ti** most efficient at lower additions: Alloys with 0.2–0.6% Ti better than those with 2% Ti; **Zn-3Al-2Mg-0.2Ti** 2-fold better than Zn-3Al-2Mg
- **Mo**: Surprisingly strong effect of 0.01 % Mo in Zn-Mg-Mo and Zn-Al-Mg-Mo; **Zn-3Al-2Mg-0.01Mo** 1.5-fold better than Zn-3Al-2Mg
- **Mn**: Best improvement for **Zn-3Al-2Mg-0.2Mn**; further increase in Mn content worsen the stability
- **Cr, Mm (Ce), Si**: **Most promising**

# Stage A+B: ECC1, photos

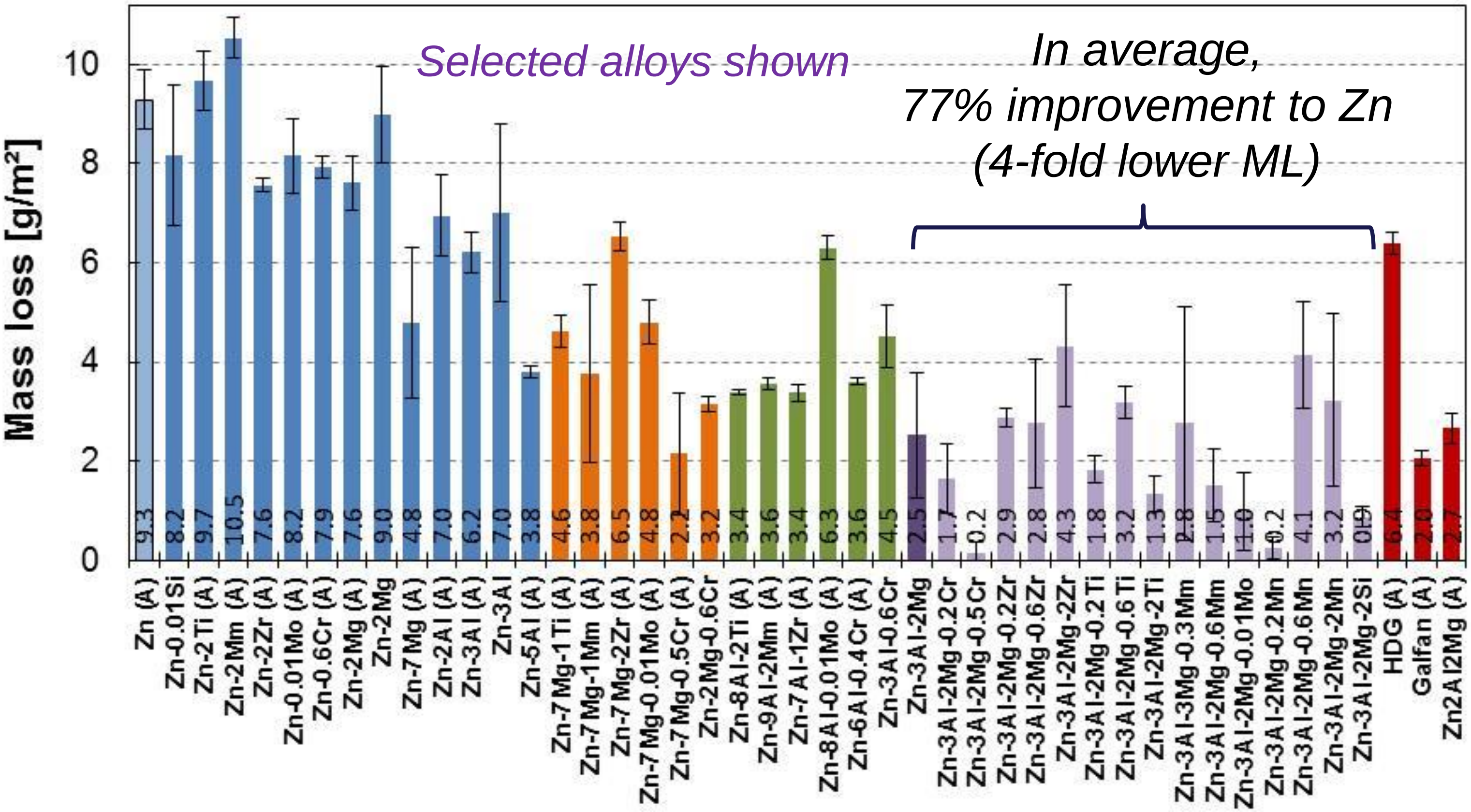




*Zn* | *Zn-3Al-2Mg-0.5Cr* | *Zn-3Al-2Mg-0.6Mm*

# Stage A+B: Static $SO_4^{2-}$ / $Cl^-$

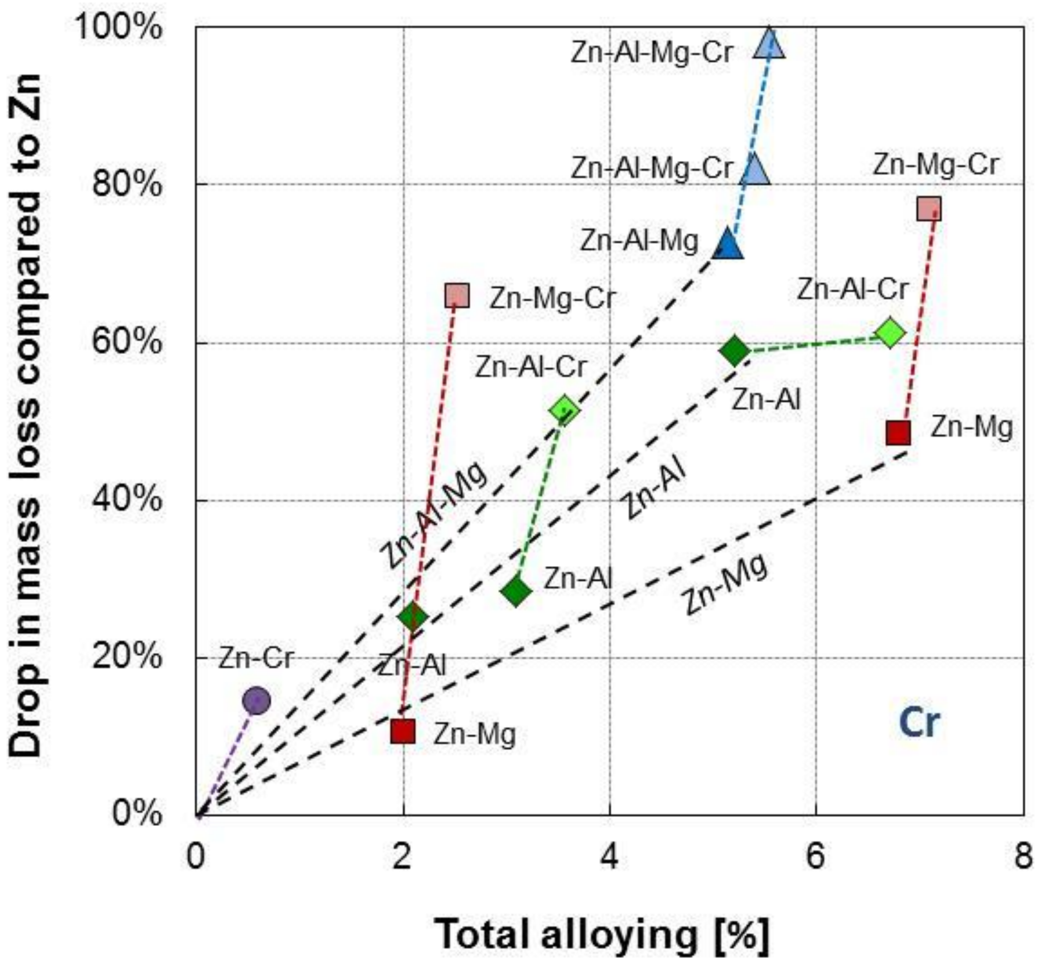
- Contamination with of 0.7 g/m² chloride (NaCl) and 0.7 g/m² sulphate ($Na_2SO_4$)
- Climatic chamber at **20 °C, 85 % RH for 4 weeks**



# Stage A+B: Static exposure



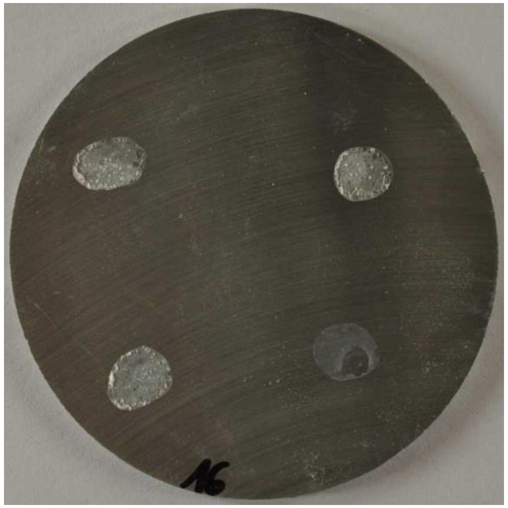
- Al seems to be more efficient than Mg and synergy between Al and Mg exists
- With minor exceptions, the same trends as in ECC1 observed



# Stage A+B: Spreading test

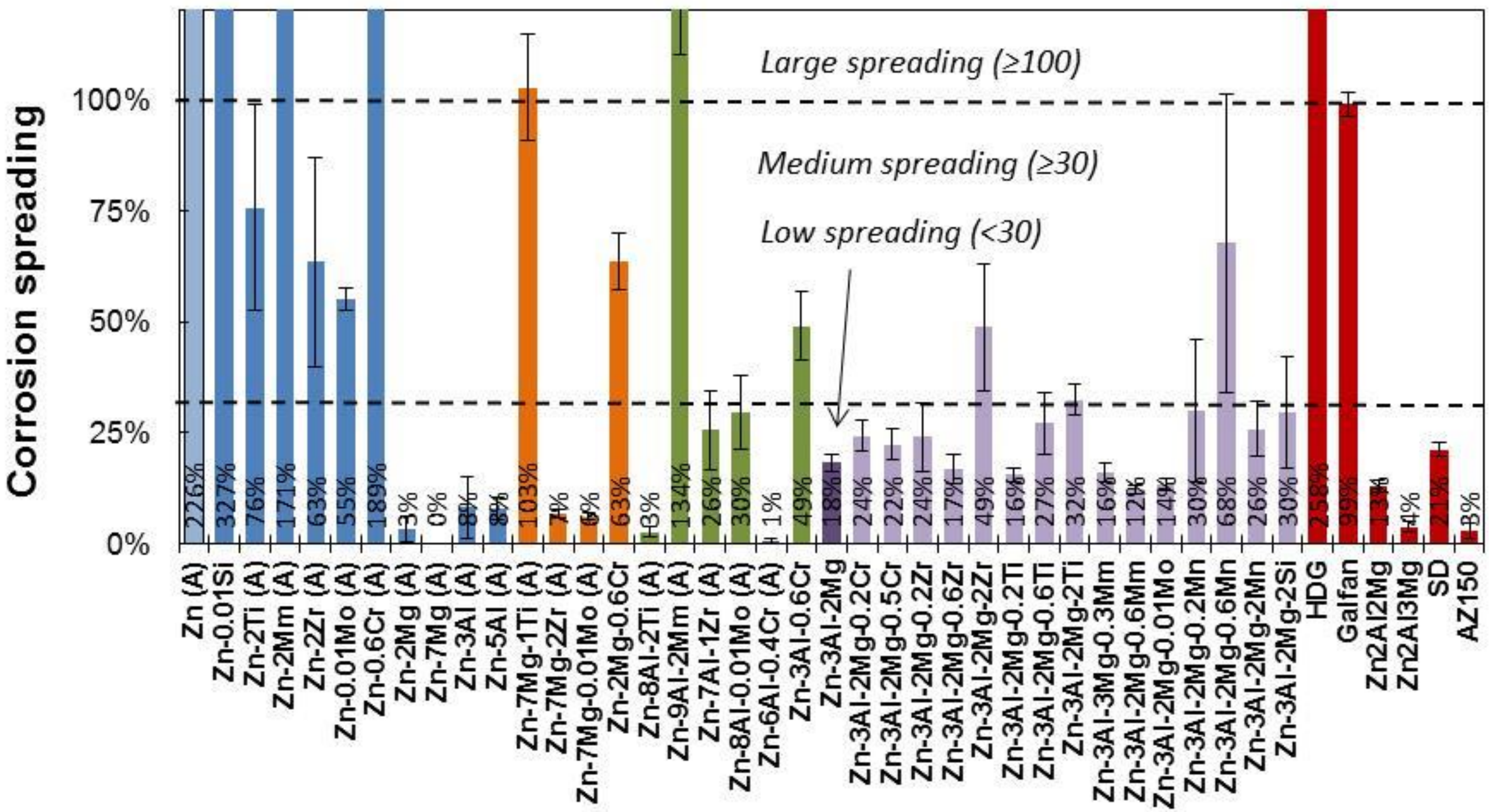


- 3 25-µl droplets of 0.5 M NaCl deposited on surfaces polished to grit 360 and degreased in acetone
- Samples pre-heated to 40 °C to speed up drying
- Exposure at 20 °C and at 95 % RH for 24 hours
- Droplet area measured before (≈ 26 mm²) and after exposure
- The spreading in humid air provides information on the corrosion activity of the surface
- Cathodic reaction takes usually place outside the original droplet area



# Stage A+B: Spreading test






*Selected alloys shown*

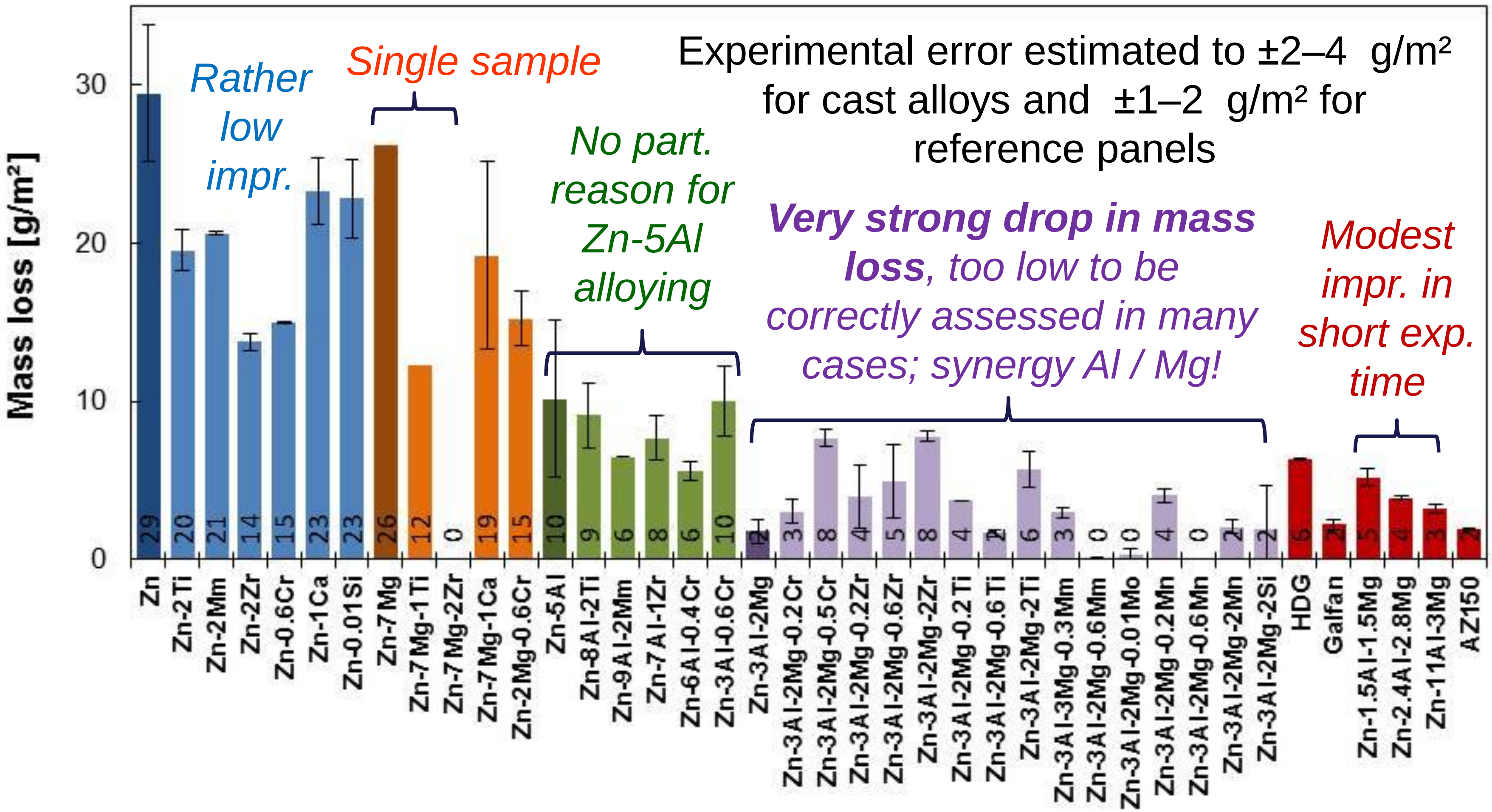
Binary alloys: Only Al and Mg efficient
Ternary alloys: Large differences, often worse than Zn-Al and Zn-Mg
Quaternary Zn-3Al-2Mg-X alloys: Generally good performance

# Stage A+B: Field exposure



- Selected alloys from Stage A with better results and all alloys from Stage B
- Marine site in Brest, C5M for steel, 45° S
- 4 samples of each alloy fixed on plastic support + reference panels (edges masked)
- Start: 23/11/2012, 2 samples removed on 09/10/2013 ⇨ Mass loss & corrosion depth

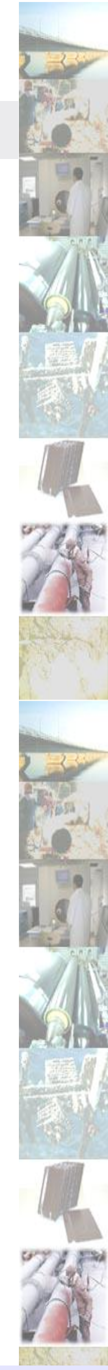

# Stage A+B: Field, mass loss



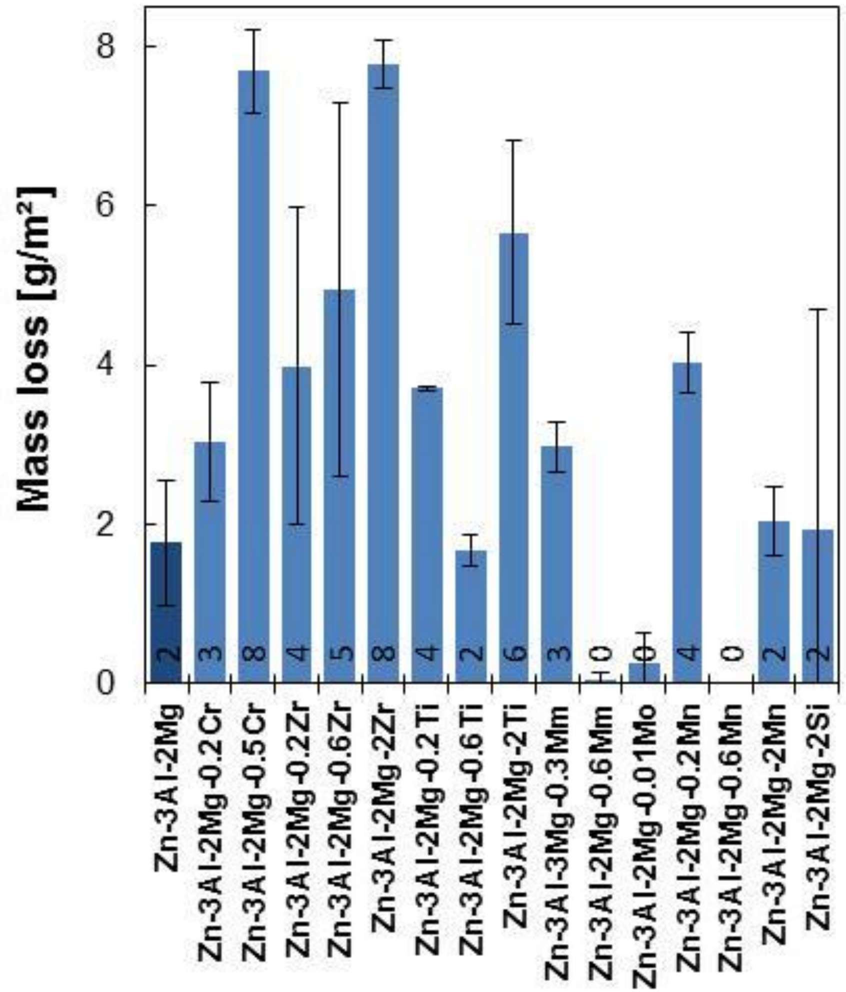

Huge difference between cast Zn and HDG; stronger effect of X in binary alloys than in accelerated tests; Zn-7Mg worse outdoors than in accelerated tests

# Stage A+B: Field, mass loss



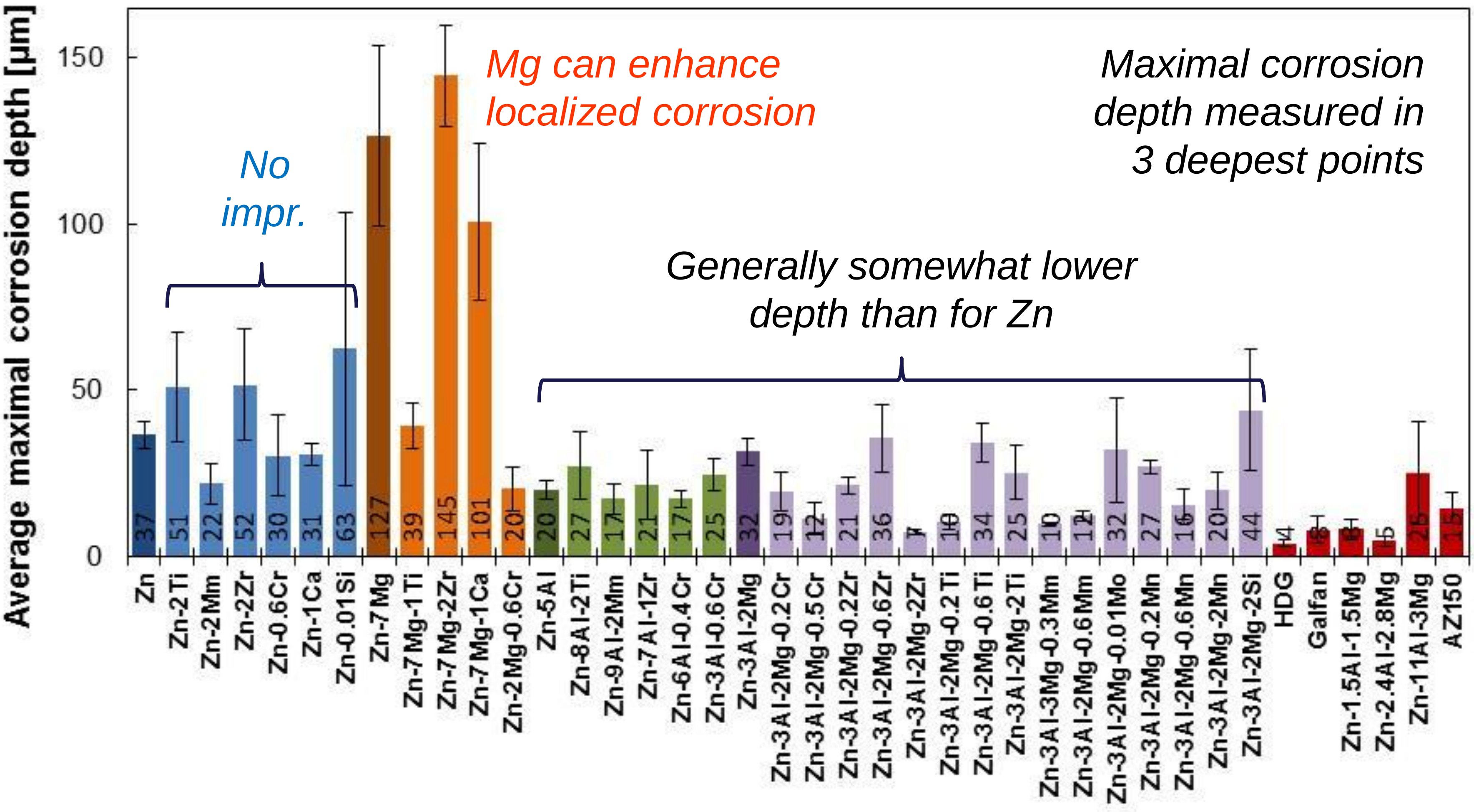


- **Cr**: Efficient in binary and ternary alloys, no improvement in Zn-3Al-2Mg
- **Zr**: No improvement in Zn-3Al-2Mg, efficient in Zn-Zr and Zn-Mg-Zr (to be verified)
- **Ti**: More efficient in lower additions up to 0.6 wt.%
- **Mm (Ce)**: Great stability at 0.6 wt.%
- **Mo**: Very good stability
- **Mn**: Best results for Zn-3Al-2Mg-0.6Mn
- **Si**: Good results, large difference between 2 samples




**Longer-term data necessary for these materials with high stability**

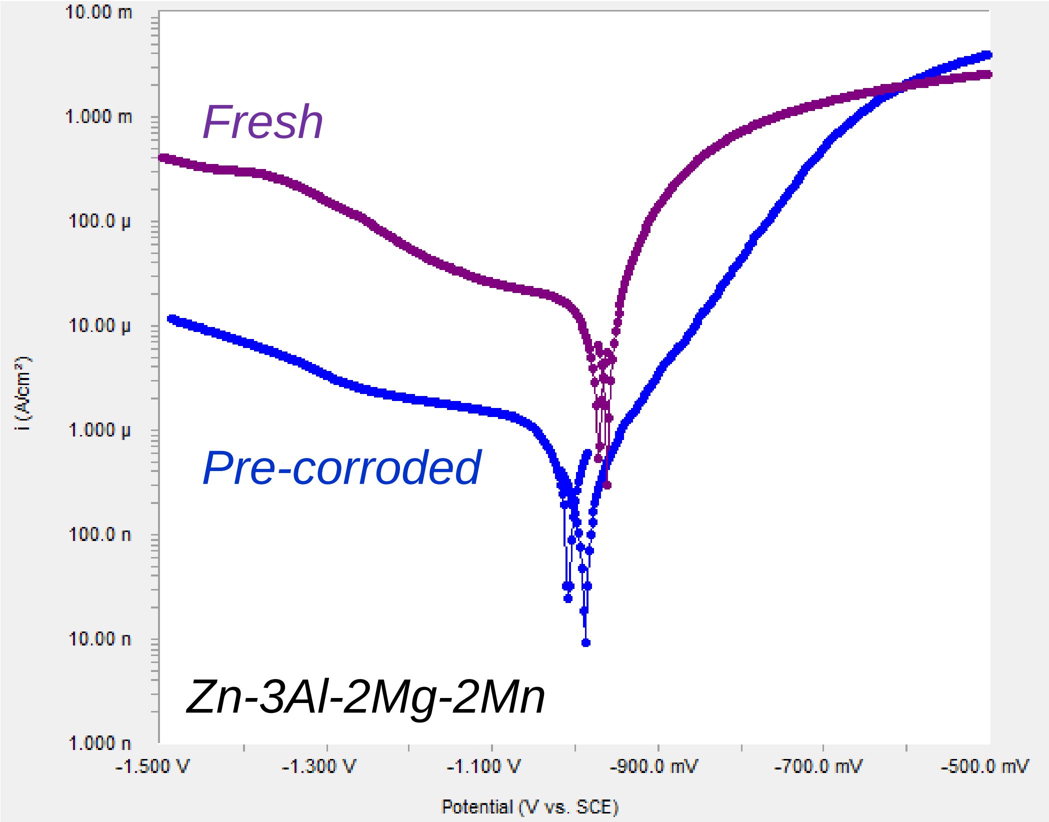
# Stage A+B: Field, depth




Mg-rich phases corrode preferentially and the attack became more localized; Al seems to compensate this effect

# Stage A+B: Field, PTD curves

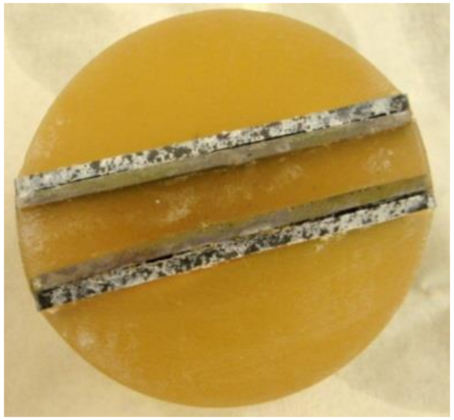
- Potentiodynamic curves in artificial rain water
  - Fresh surface
  - After exposure at the marine site for 10 months
- Protective corrosion products significantly (2-orders of magnitude) reduce cathodic current, drop in anodic current too
- Similar effect for most compositions

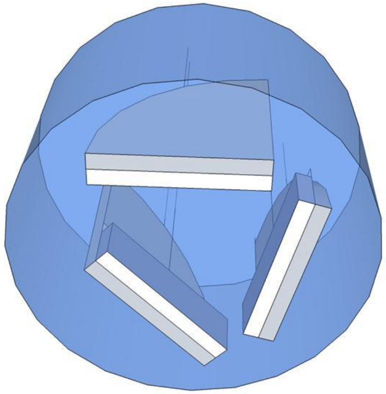
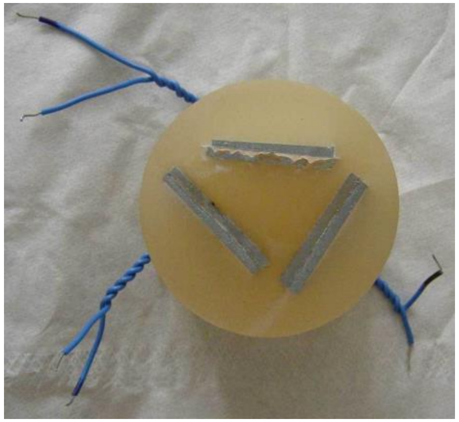



# Stage A+B: Galvanic protection

- Corrosion potential of galvanic coating must be negative to that of steel to provide galvanic protection
- Electrochemical measurements in artificial rain water and in humid air, red rust formation →

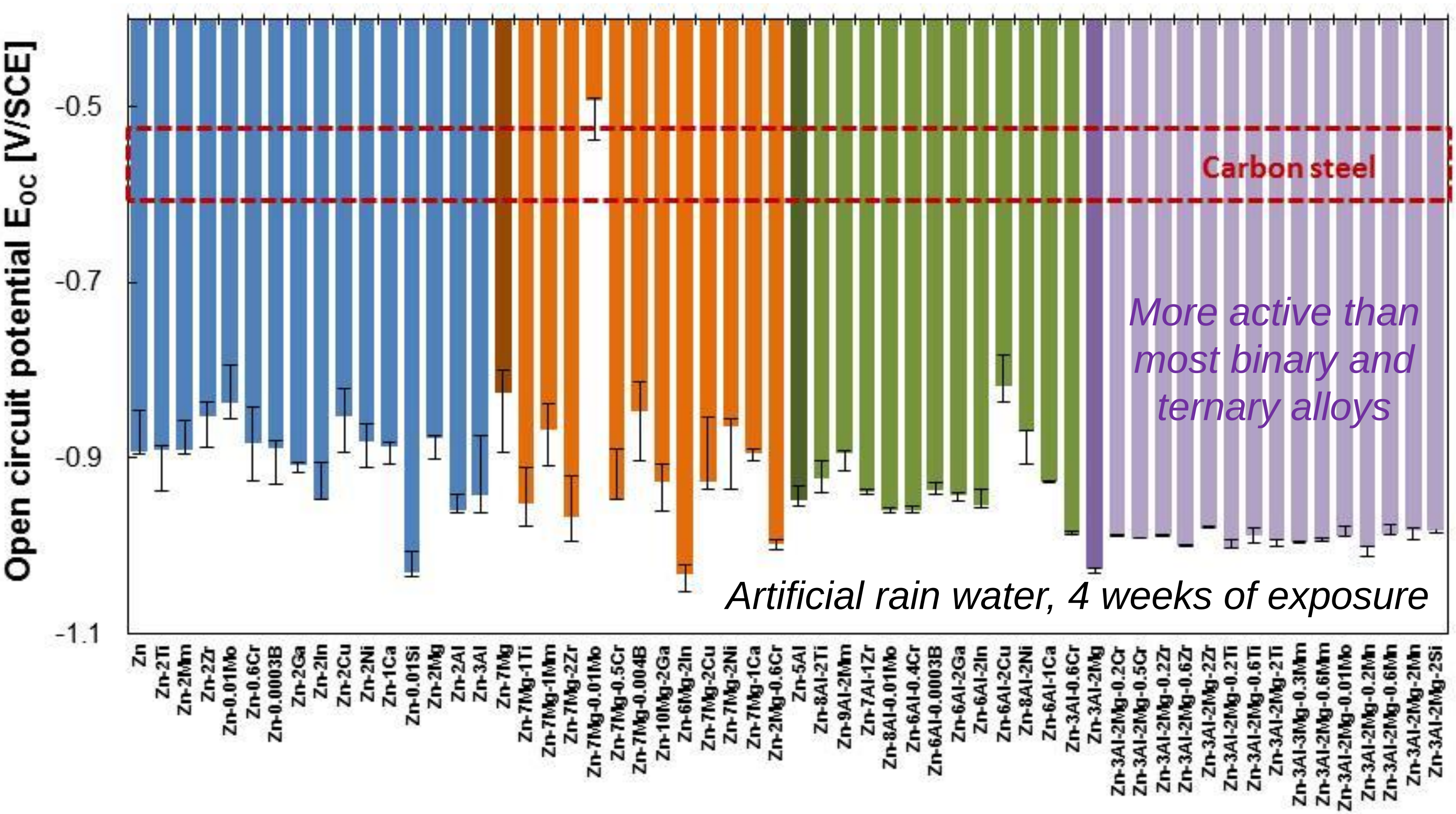
| Salt | Content (mg/L) |
|---|---|
| $Na_2SO_4$ | 852 |
| $MgCl_2$ | 4.3 |
| $CaCl_2$ | 3.1 |
| NaCl | 8.9 |
| $NH_4NO_3$ | 10.5 |



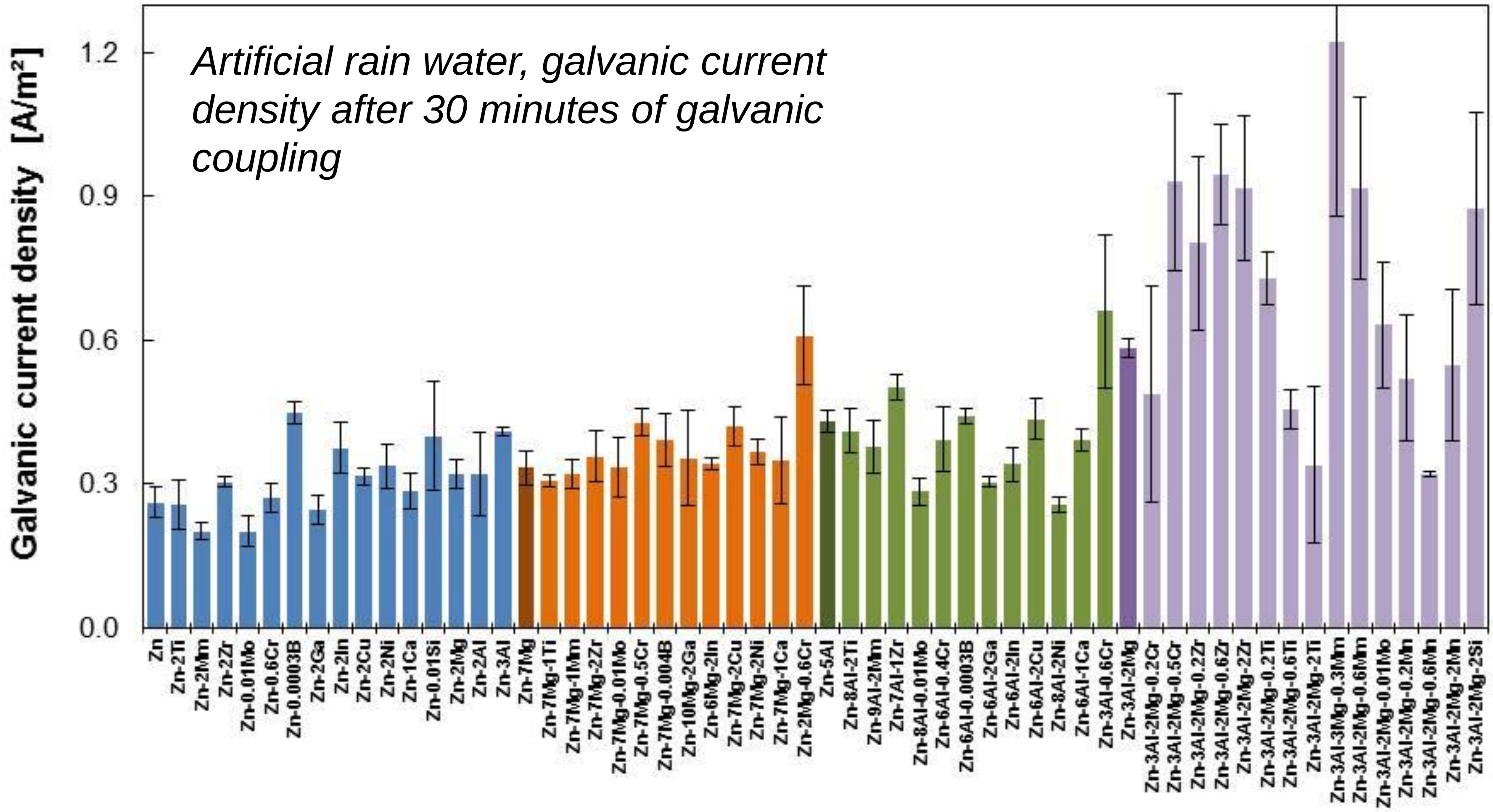
# Stage A+B: $E_{OC}$, rain water






Except for Zn-7Mg-0.01Mo, all alloys were safely anodic to steel even after 4 weeks of galvanic coupling in artificial rain water

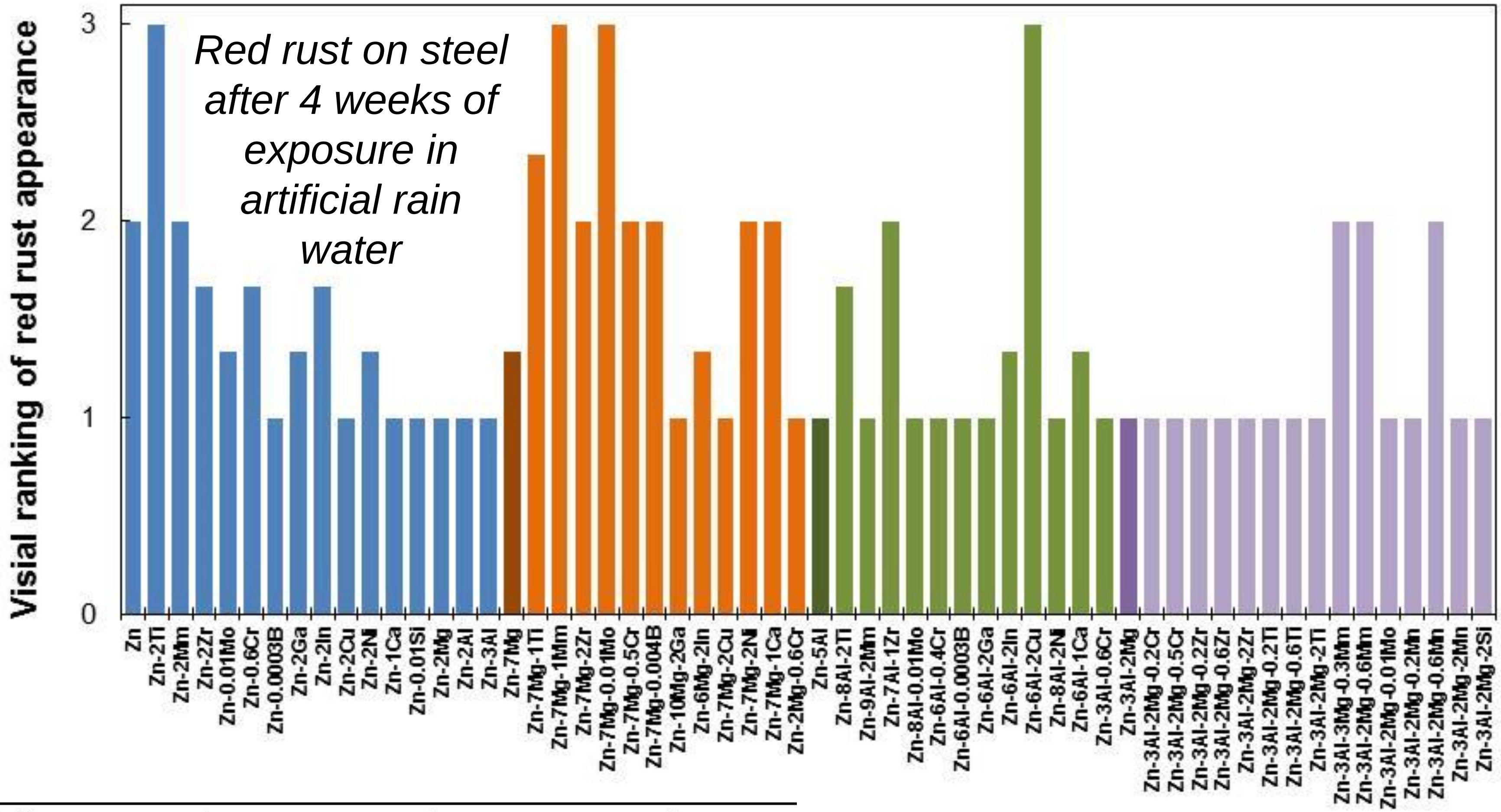
# Stage A+B: $I_{GALV}$, rain water




Most materials provided **higher galvanic current than zinc**; similar data obtained after 4 weeks of coupling (except for Zn-7Mg-0.01Mo)

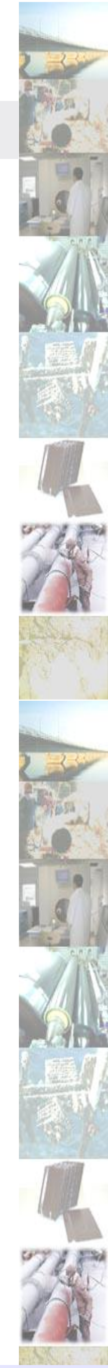
# Stage A+B: Red rust, rain water





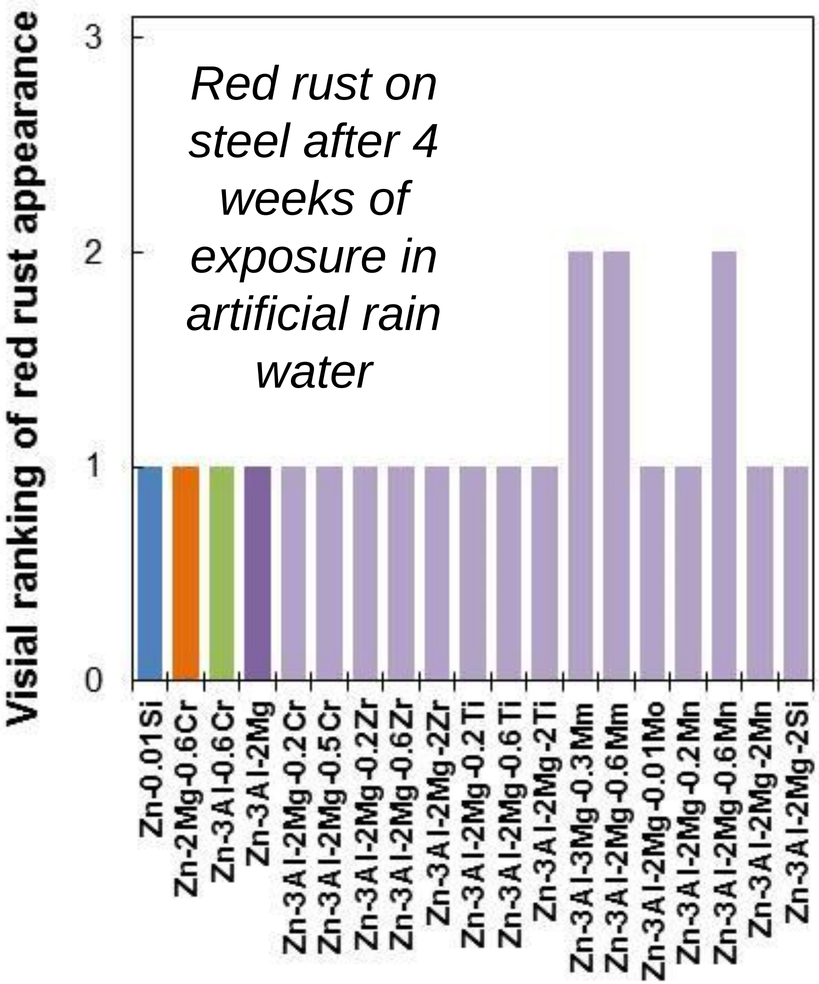

| Ranking | 1 | 2 | 3 |
|---|---|---|---|
| Description | No red rust | Slight red rusting | Heavy red rusting |
| Examples | | | |

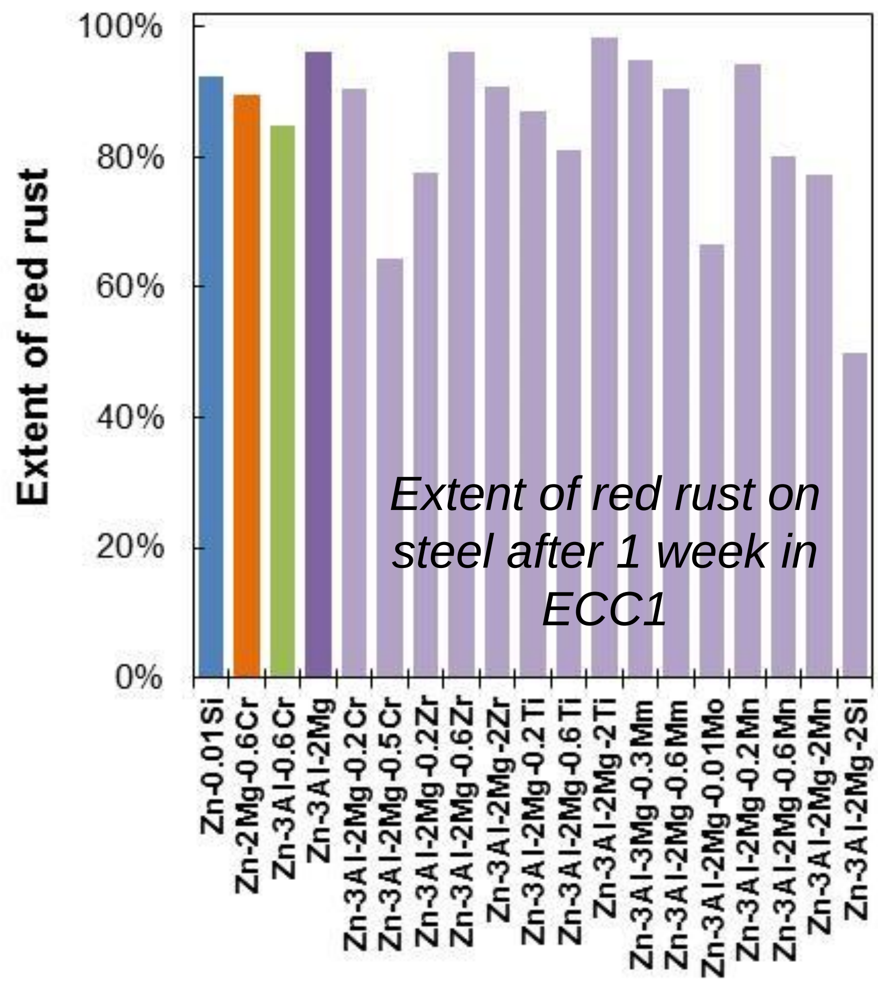
No red rust on most materials; Zn-Al-X and Zn-Al-Mg-X the best

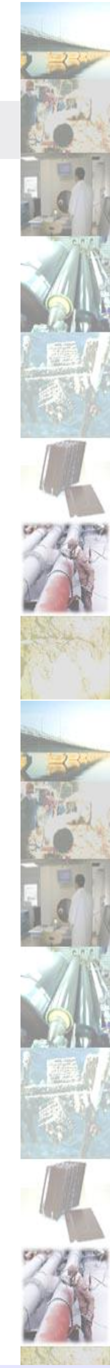


# Stage B: Red rust





With a few exceptions, similar performance of Zn-3Al-2Mg-X materials

# Summary open: Improvement



## Accelerated tests

**Mean improvement to Zn**

| Material | | Impr. |
|---|---|---|
| Zn-3Al-2Mg-2Si | ✶ | 80% |
| Zn-3Al-2Mg-0.5Cr | | 79% |
| Zn-3Al-2Mg-0.2Mn | ✶ | 74% |
| Zn-3Al-2Mg-0.01Mo | ✶ | 74% |
| Zn-3Al-2Mg-0.2Ti | ✶ | 74% |
| Zn-3Al-2Mg-0.6Ti | ✶ | 70% |
| Zn-3Al-2Mg-0.6Mm | ✶ | 69% |
| Zn-3Al-2Mg-2Ti | | 69% |
| Zn-3Al-2Mg-0.2Cr | ✶ | 69% |
| Zn-3Al-3Mg-0.3Mm | ✶ | 63% |
| Zn-3Al-0.6Cr | | 63% |
| Zn-3Al-2Mg-2Mn | ✶ | 63% |
| Zn-6Al-0.4Cr | ✶ | 63% |
| Zn-3Al-2Mg-0.6Zr | | 63% |
| Zn-3Al-2Mg | ✶ | 62% |

*Results of ECC1, static test, spreading test and galvanic protection weighed and combined*

## Field exposure

**Mean improvement to Zn**

| Material | Impr. |
|---|---|
| Zn-3Al-2Mg-0.6Mm | 95% |
| Zn-3Al-2Mg-0.6Mn | 94% |
| Zn-3Al-3Mg-0.3Mm | 87% |
| Zn-3Al-2Mg-0.01Mo | 86% |
| Zn-3Al-2Mg-2Mn | 86% |
| Zn-3Al-2Mg-0.2Ti | 85% |
| Zn-3Al-2Mg-0.2Cr | 83% |
| Zn-3Al-2Mg | 82% |
| Zn-3Al-2Mg-0.6Ti | 81% |
| Zn-3Al-2Mg-0.2Zr | 80% |
| Zn-3Al-2Mg-0.2Mn | 77% |
| Zn-6Al-0.4Cr | 77% |
| Zn-3Al-2Mg-2Si | 76% |
| Zn-3Al-2Mg-2Zr | 75% |
| Zn-9Al-2Mm | 74% |

*Mass loss and corrosion depth data weighed and combined*

✶ *Very good also at the marine site*

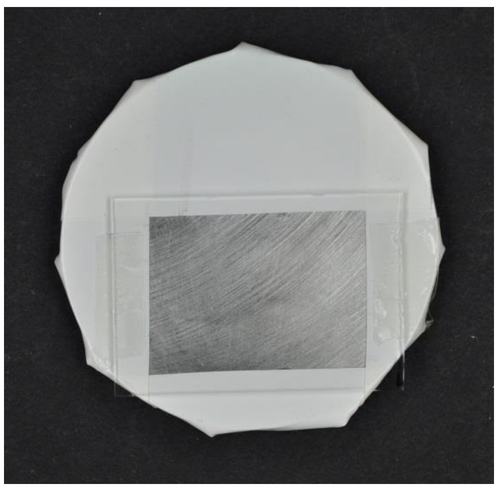
# Summary open surface

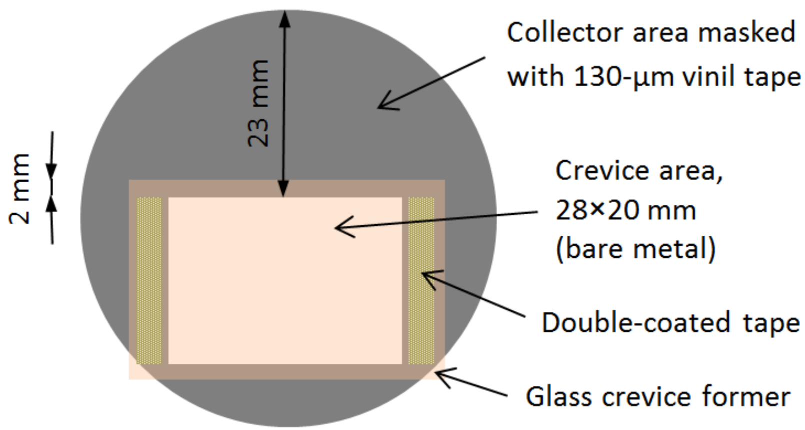


- Corrosion assessment of over 50 compositions done, but the field data must be considered as preliminary ⇨ Longer exposures necessary
- **Alloys based on Zn-3Al-2Mg most stable** due to strong inhibition potential of Al and Mg (*outside this family, only Zn-(3-6)Al-0.4Cr successful*)
- It is **advantageous to combine Al and Mg**, especially in marine exposure conditions
- Small additions of **Ce (Mm), Cr, Si, Mn, Mo, Ti, Zr can increase corrosion stability**, mostly at lower concentrations up to 0.6 wt.%; however, is the improvement strong enough to be interesting?

# Stage C: Crevice / hem flange

- Corrosion in confined zones of hem flanges often critical for car bodies
- Crevice samples of selected materials from Stage A and B exposed for 6 weeks in ECC1, 4 replicates

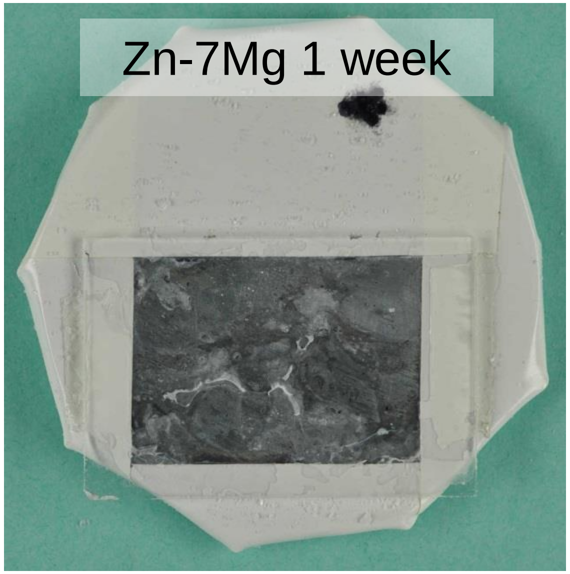


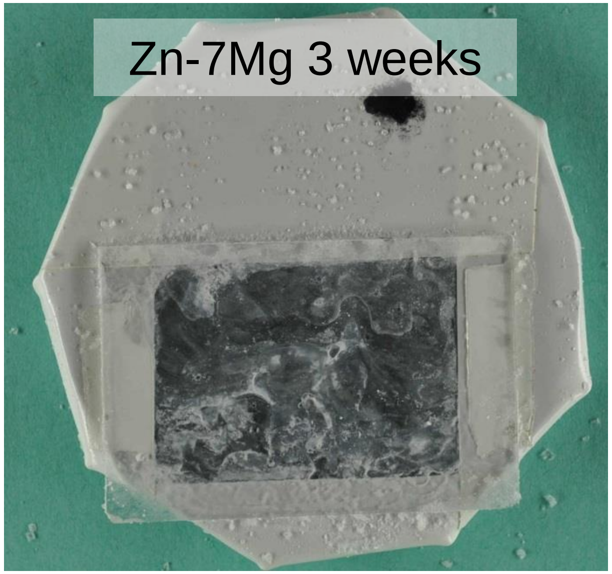



Ø 50 mm
**Opening width**: 130 µm
**Crevice width**: 260 µm
*Filled with NaCl solution before the exposure*

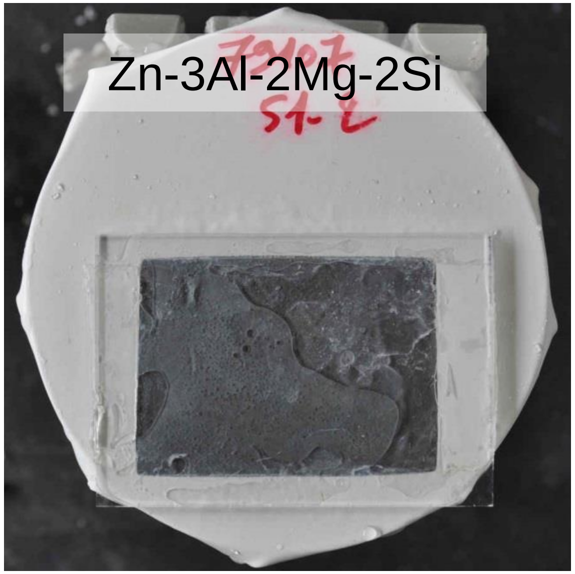
- Design not fully ideal due to small sample size (small collecting area, small crevice area)

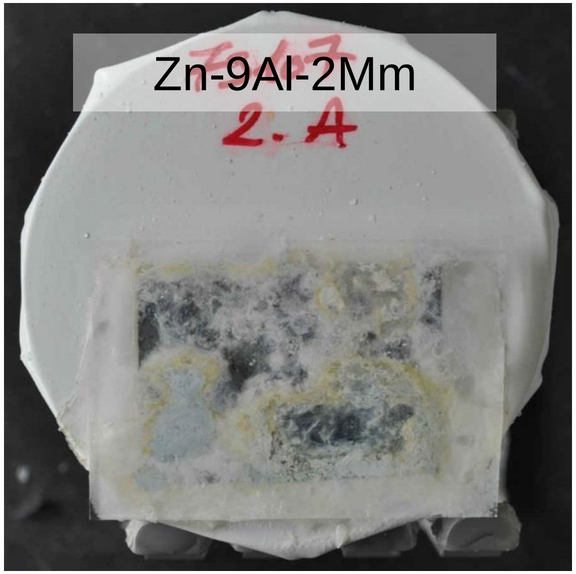
# Stage C: Crevice, appearance

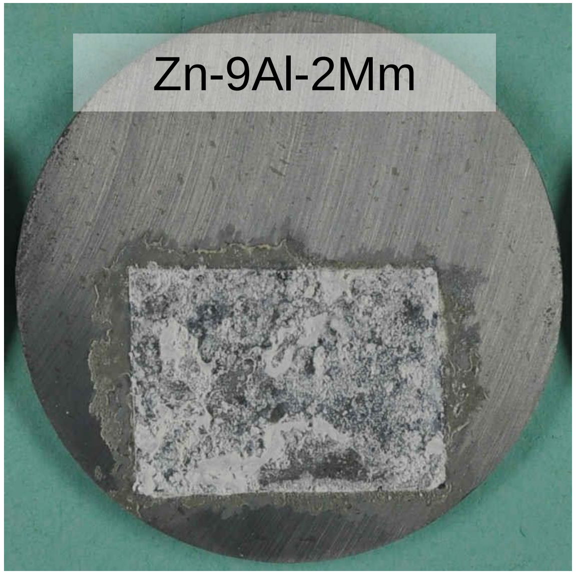




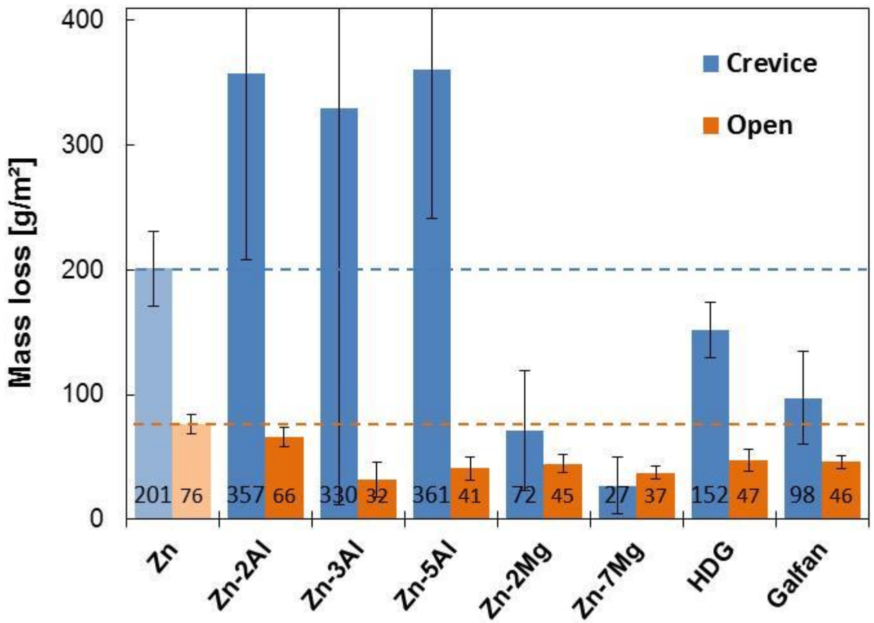


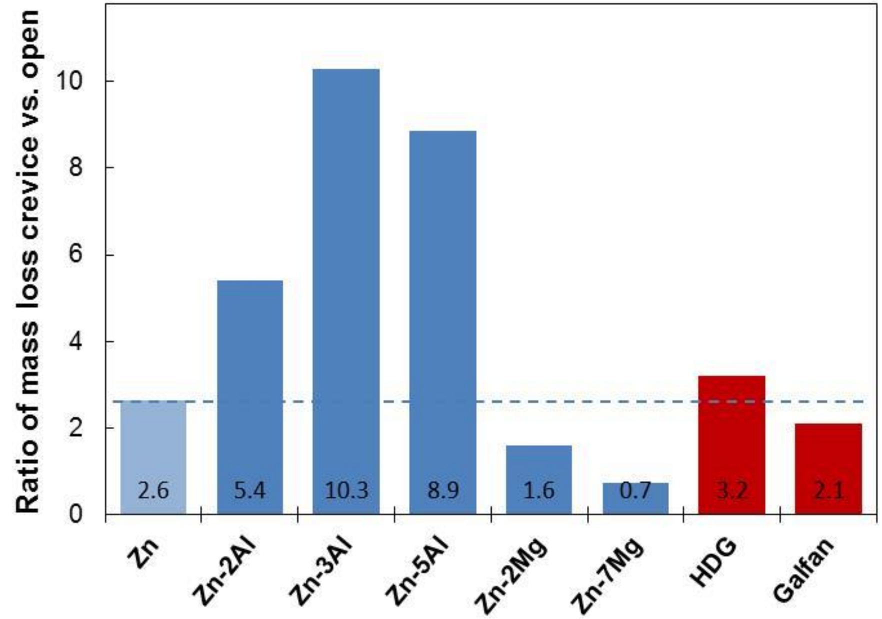



# Stage C: Crevice, mass loss





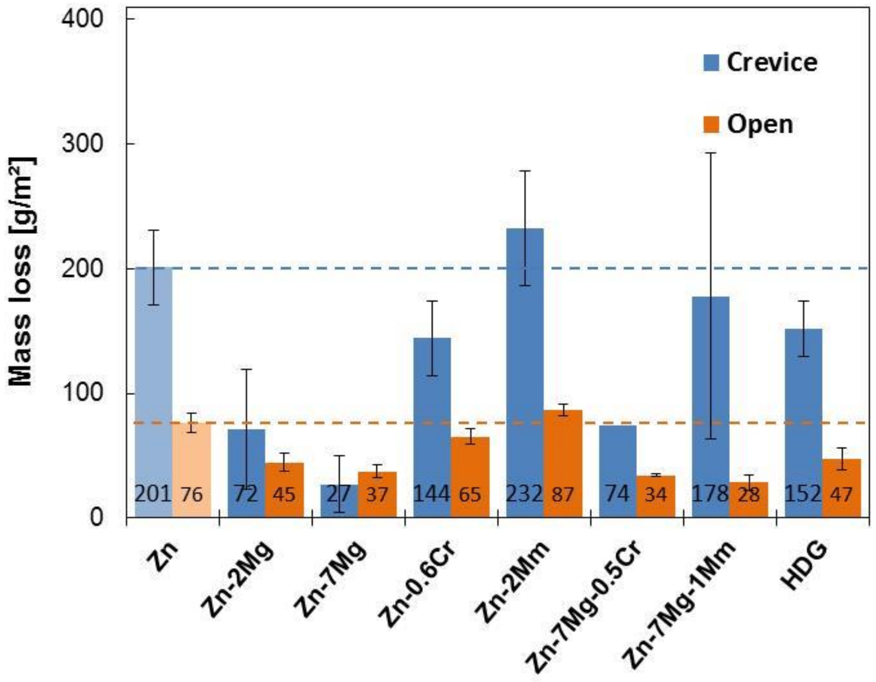



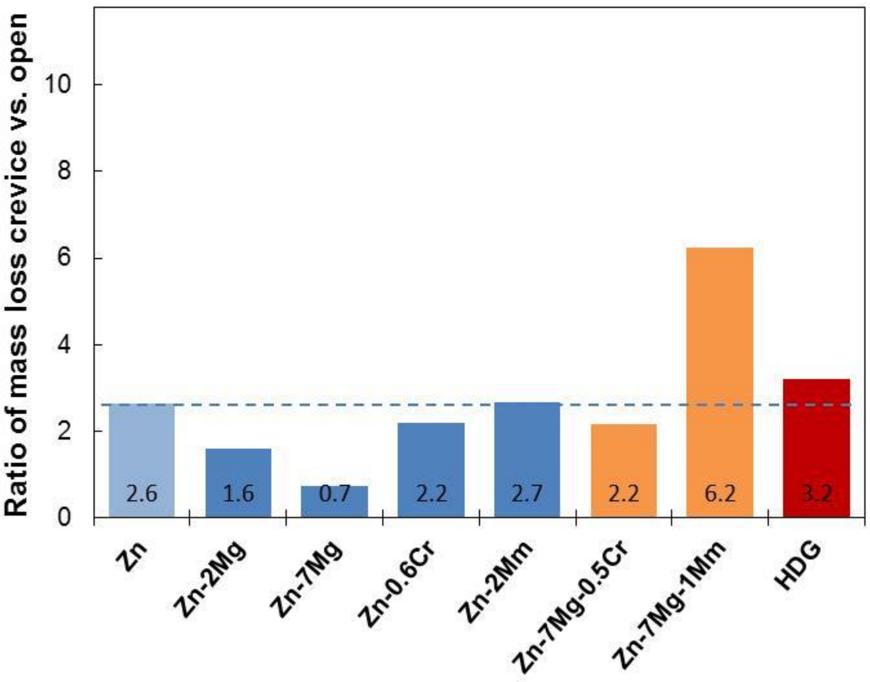

- **Effect of Al and Mg different in open and crevice configuration**
- Corrosion acceleration in crevice **strongly inhibited by Mg** and **enhanced by Al**
- Why Galfan and Zn-5Al so different in crevice?

# Stage C: Crevice, mass loss



- Can any other element further improved the performance of Zn-Mg in crevices?



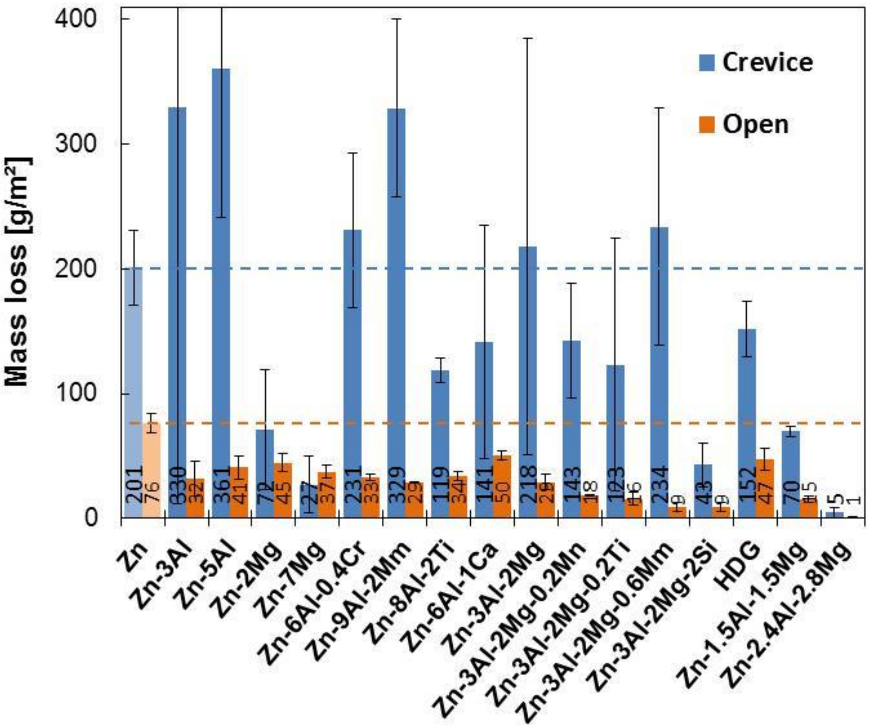



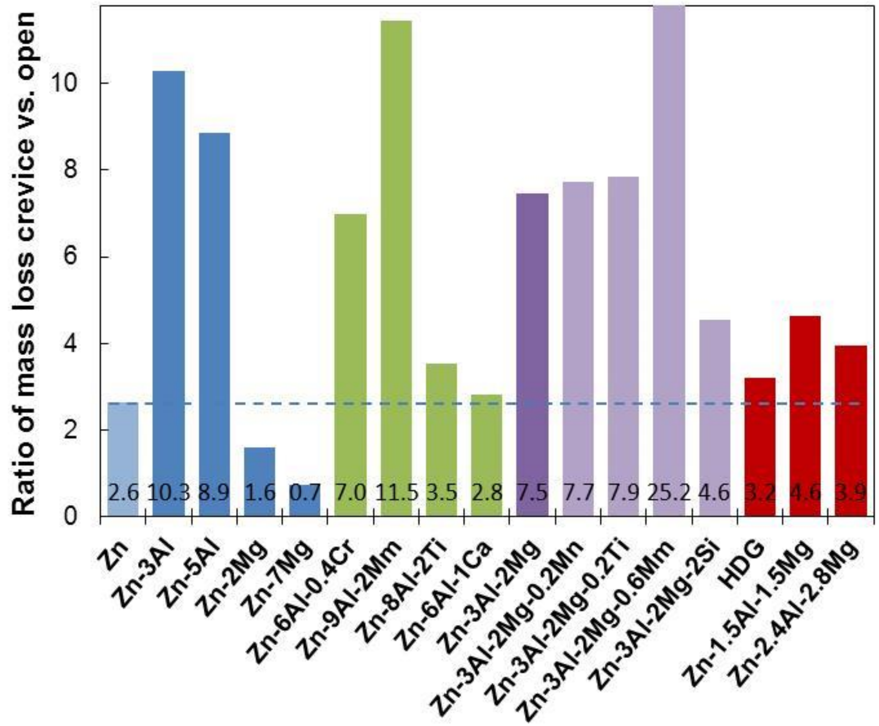

- Cr and Ce (Mm) have neutral (Zn-X) to negative (Zn-Mg-X) effect on corrosion in confined zones

# Stage C: Crevice, mass loss

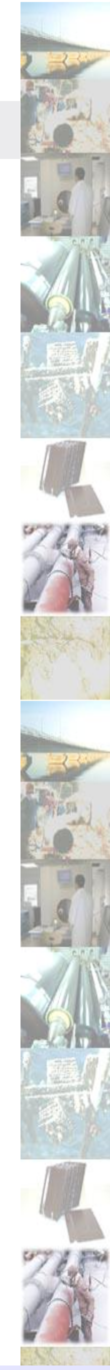


- Can any other element limit the negative effect of Al?




- Si, Ti and possibly Mg and Ca seem to inhibit corrosion in confined zones in presence of Al



# Summary confined zones

- **Effect of alloying elements different in open and crevice configuration**
- Preliminary results:

| Element | Open | Crevice |
|---|---|---|
| Al | Positive | Negative |
| Mg | Positive | Strongly positive without Al, slightly positive with Al |
| Cr | Slightly positive | Mostly neutral |
| Mm (Ce) | Positive to slightly negative | Neutral to negative |
| Ti | Slightly positive | Possibly positive (with Al or at higher concentration) |
| Ca | Slightly negative | Possibly positive (with Al) |
| Mn | Slightly positive | Neutral |
| Si | Positive | Positive (with Al) |

*Positive = Inhibition of corrosion; Negative = Increase in mass loss*

- Composition with good performance in both open and crevice configuration needs to be identified

# Conclusions

- On **open surfaces**, **mixture of Al/Mg beneficial**
- **Alloys based on Zn-3Al-2Mg most stable**
- All alloys except Zn-7Mg-0.01Mo **galvanically protect steel** similarly or better than zinc
- **Strong inhibition with Mg and detrimental effect of Al in confined zones** ⇨ Alloys with low content of Al or addition of X to be considered
- Compositions with good performance in open configuration identified, the same needs to be done for confined zones

# Stage C: New alloys



- Prepare new alloys, step 1:
  - **Zn-3Al-2Mg-0.2Si, Zn-3Al-2Mg-0.6Si**: What Si concentration is optimal?
  - **Zn-1Al-2Mg, Zn-2Al-2Mg, Zn-2Al-3Mg**: Is it possible to limit the detrimental effect of Al in crevices by lowering the Al/Mg ratio?
  - **Zn-3Al-2Mg-0.2Ca, Zn-3Al-2Mg-0.6Ca**: Can calcium improve the performance of Zn-Al-Mg in crevices?
- Step 2:
  - **Zn-1Al-2Mg-xSi, Zn-2Al-2Mg-xSi**: Lower Al and Si addition should improve stability in crevices.
  - **Zn-5Al-2Mg, Zn-5Al-2Mg-xSi**: Why Galfan performed well in the crevice test? Microstructure?
  - Concentration of Si to be selected after Step 1

# Stage C: Work plan



- Step 1 materials finished on 01/11/2014, now:
  - **Characterization** in the same extent as in Stage A, B
  - **Corrosion performance in open configuration**: ECC1, static, spreading tests, field exposure
  - **Corrosion in confined zones**, together with further materials of interest from Stage A and B
  - **Galvanic corrosion study**, simplified
  - *End: January 2014*
- Step 2 materials, preparation and characterization: *January–April 2014*
- Further experiments on **mechanism,** paper on principal results: *Until April 2014*

# Project proposal 2014–2016

- Focus on **coatings** prepared by hot dipping
- Compositions to be selected after end of Stage C taking into account also technical, environmental and economical aspects
- General corrosion stability (cosmetic corrosion), protection in confined zones, corrosion at cut-edges, corrosion depth, temporary corrosion protection, time to white/red rust formation, paint stability, formability, …