Evaluation of Chloride-induced Corrosion in Reinforced Calcined Clays and Volcanic Ashes Based Alkali-activated Concretes

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Background & Motivation

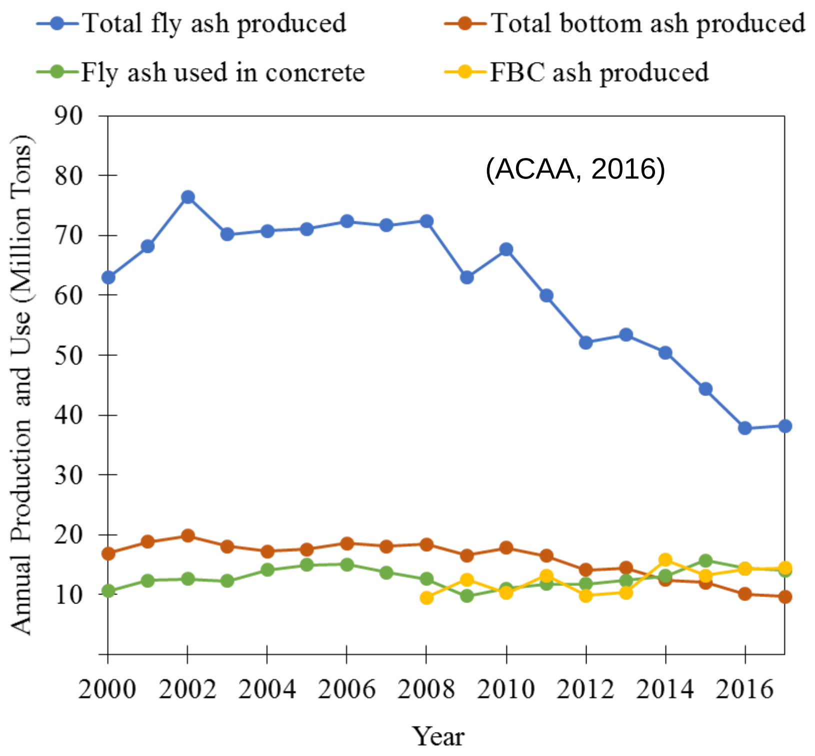
- By 2025, global cement demand - 4.7 billion metric tons (an increase of 2.9% per year).

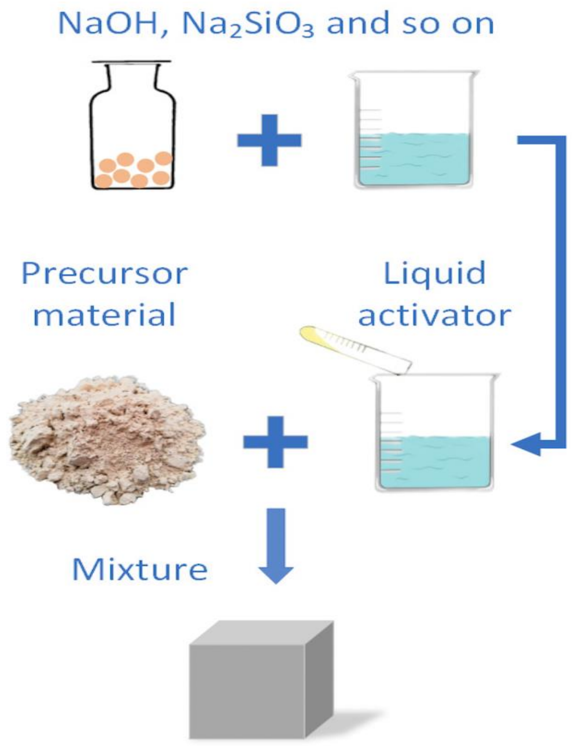
- Low environmental impact binders– Alkali-activated materials

- Fly ash and GGBS – popular precursors

- Rapid decommissioning of thermal power plants in and competitive use of Slag as SCMs.

- **Calcined clays** and **volcanic ashes-** an emerging unconventional precursor for Alkali activated systems.

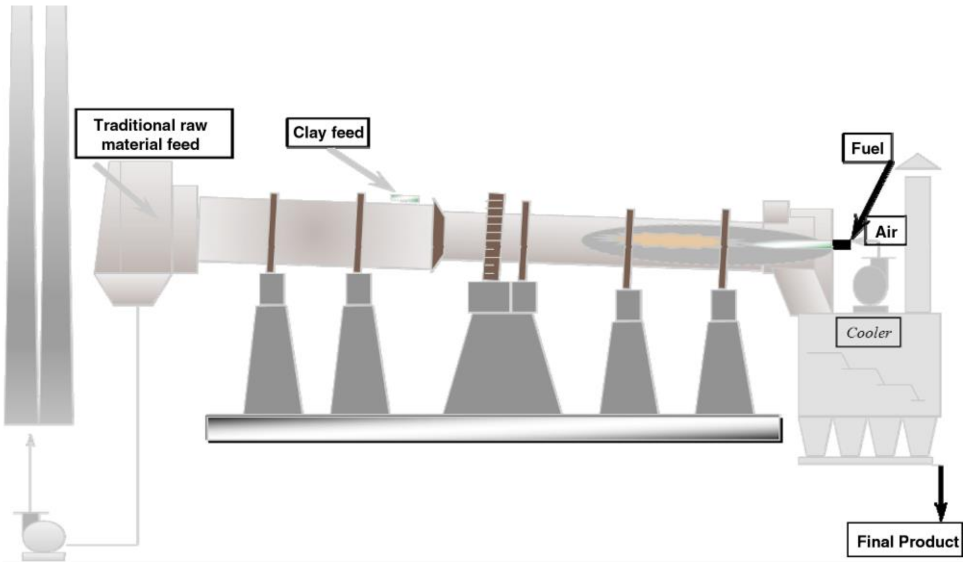




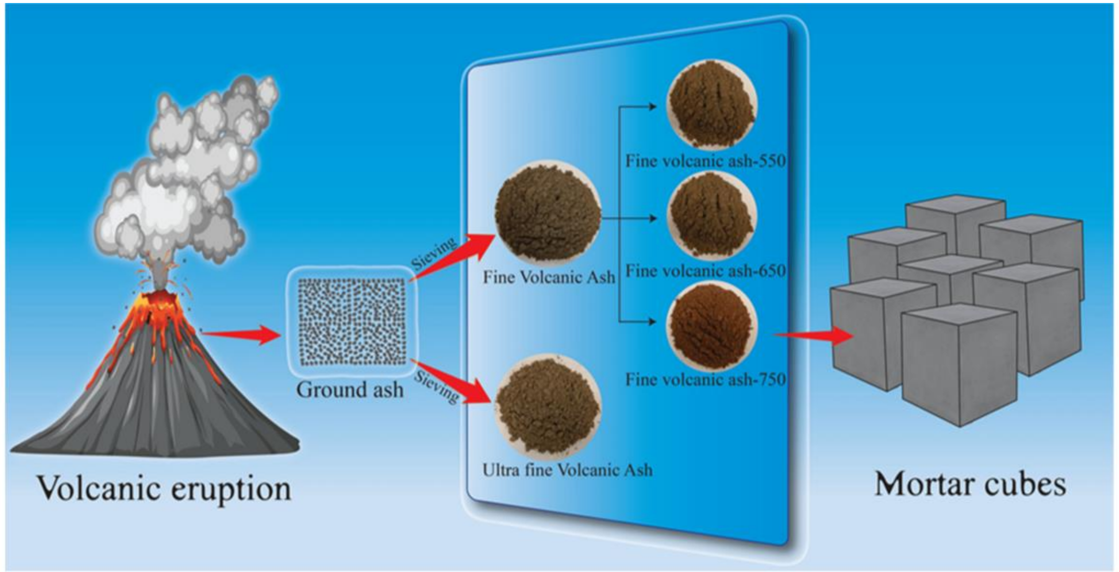
Alkali Activated concrete

Qin et al (2022)

Non-traditional Precursors



Almenares et al. (2017), Case studies in Construction materials



Khan et al. (2022) Crystals

- Investigate chloride-induced corrosion resistance in calcined clay and volcanic ash-based alkali-activated concrete via potentiodynamic tests.
- Examine the compatibility of current standard specifications, primarily designed for OPC-based binders, when applied to alkali-activated Calcined clay and Volcanic ash-based concrete(AAC).

Materials - Binders

Calcined Clays (CC)

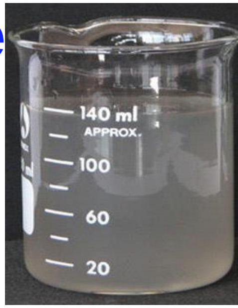
3 kaolinite-based clays (calcined at 750^{0}C) and ground to acquire a reactive form of clay.

Volcanic ash (VA)

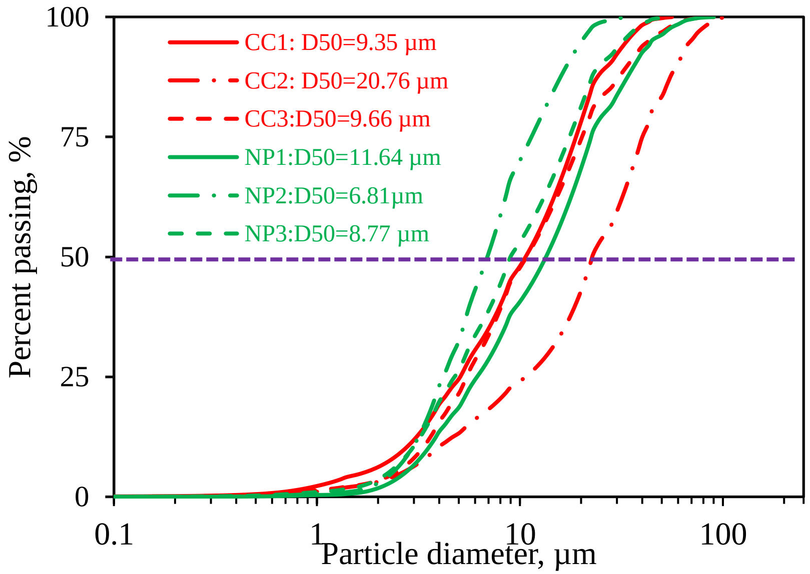
3 types of ground volcanic ashes of obsidian, pumice, and pumiceous tuff.

Activator Solution:

Hybrid solution of sodium hydroxide and sodium silicate



Material ID	CC1	CC2	CC3	VA1	VA2	VA3
SiO_2 (%)	56.0	56.3	54.4	72.0	72.4	70.4
Al_2O_3 (%)	25.02	34.89	36.83	12.13	11.50	12.83
Fe_2O_3 (%)	14.55	2.68	0.74	0.82	1.34	2.0
CaO (%)	0.06	0.32	0.08	0.72	0.84	1.91
SO_3 (%)	0.04	0.05	0.09	0.06	n/a	0.08
Na_2Oeq(%)	1.01	0.78	0.20	6.72	5.83	5.51
LOI	0.63	1.71	4.17	4.81	4.21	3.18



Materials

Concrete mix proportions:

35% paste volume

Fine aggregate (FA) / Total aggregate (TA) = 0.45 by volume

- Thapa et al.(Under review) CC and VA-based alkali-activated concretes(AACs) yielded comp. strength of about 40 MPa.

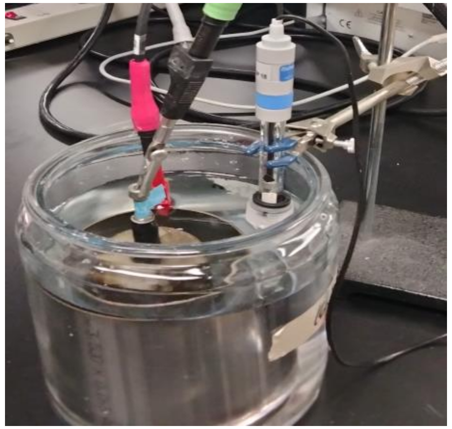
Materials	s/b	Binder (kg/m^3)	Activator (kg/m^3)	Fine aggregate (kg/m^3)	Coarse aggregate (kg/m^3)	Water (kg/m^3)
CC1	0.85	480	408	1018	1296	18
CC2	0.6		288	846	1077	16
CC3	0.9		432	1088	1385	20
VA1	0.75		360	1016	1293	19
VA2	0.75		360	1013	1290	19
VA3	0.75		360	999	1271	18
OPC	0.45	340	-	510	650	154

Activator Parameters

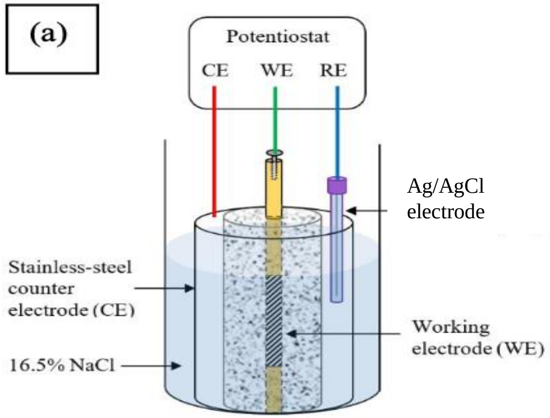
Binder	Na_2O (%)	Ms	s/b
CC1 (93% CC1 + 7%CH)	13	1.25	0.85
CC2 (97% CC2 + 3%CH)	9.25	1.25	0.60
CC3 (97% CC3 + 3%CH)	13	1.25	0.90
VA1 (63% VA1+30%CC2+7%CH)	12	1.50	0.75
VA2 (63% VA2+30%CC2+7%CH)	12	1.50	0.75
VA3 (63% VA3+30%CC2+7%CH)	12	1.50	0.75

Specimen Preparation

- Lollipop specimens 50.8 mm x 101.6 mm.
- An exposure length of 60 mm simulating a cover depth of 20 mm --> region of interest.
- Cured for 28 days
- Immersed in 16.5% NaCl (NT Build 443/ASTM C1556) solution at 23 to 25°C.



- Working electrode: rebar
- Reference electrode: Ag/AgCl electrode
- Counter electrode: stainless steel cylinder



Electrochemical Parameters / techniques

1. Open Circuit Potential (OCP) / Corrosion Potential

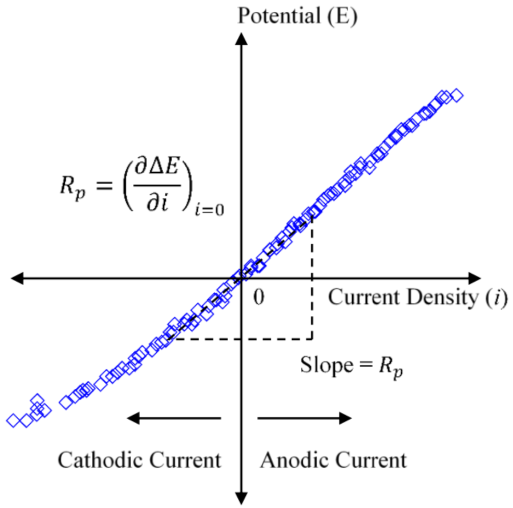
- OCP – most widely used corrosion index
- Monitored for 900 seconds

Table 1. ASTM C876-91 criteria for corrosion of steel in concrete for Ag/AgCl/1M KCl standard reference electrode

Silver/silver chloride/ 1.0M KCl	Corrosion condition
> - 100 mV	Low (10%) risk of corrosion
- 100 to -250 mV	Uncertain corrosion risk
< - 250 mV	High (> 90%) risk of corrosion
< - 400 mV	Severe corrosion (or low oxygen/water saturation)

2. Linear Polarization Resistance (Rp)

- Rp : ratio of the applied potential (E) to the resulting current density (i) in the E vs. i plot.
- ASTM G 59
- Forward scan from OCP - 30 mV to OCP+30 mV at 0.1 mV/s.

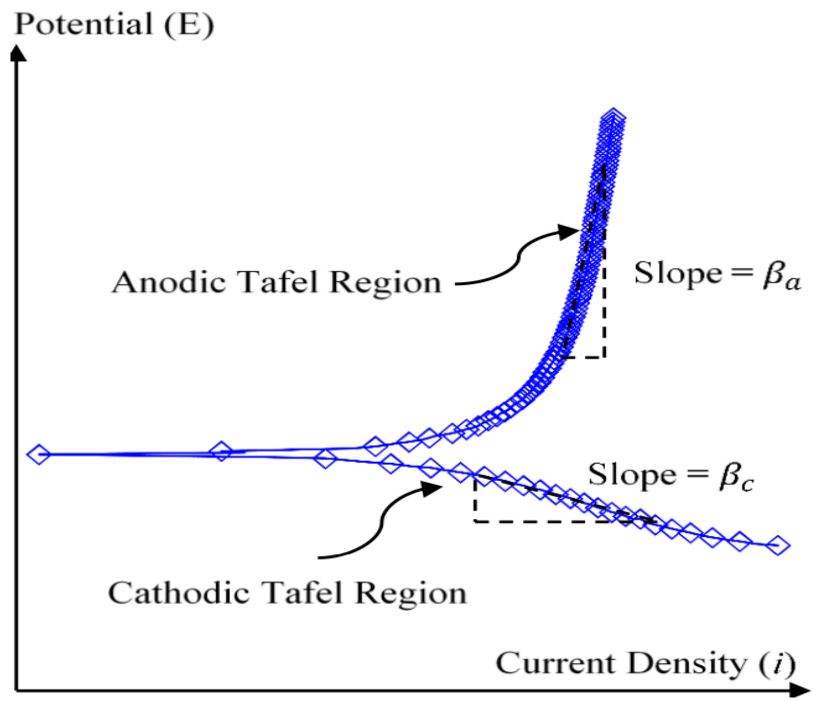


Electrochemical Parameters / techniques

- Corrosion current density (i_{corr}) – only electrochemical parameter that quantifies the rate of loss of metal
- Tafel tests were conducted to estimate B using anodic and Cathodic constants.
- Forward scan from OCP – 100 mV to OCP +100 mV at a scanning rate of 1 mV/s.

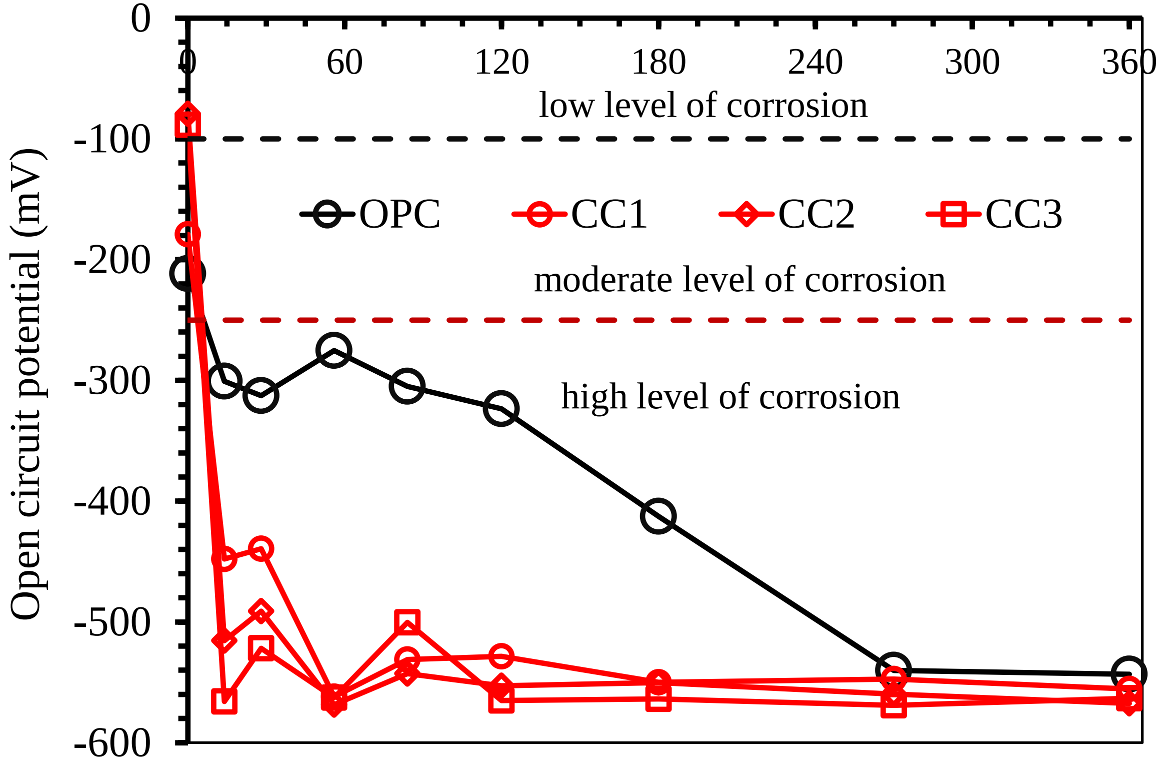
$$i_{corr} = \frac{B}{Rp} = \left[\frac{\beta_a . \beta_c}{2.303(\beta_a + \beta_c)}\right]\frac{1}{Rp}$$

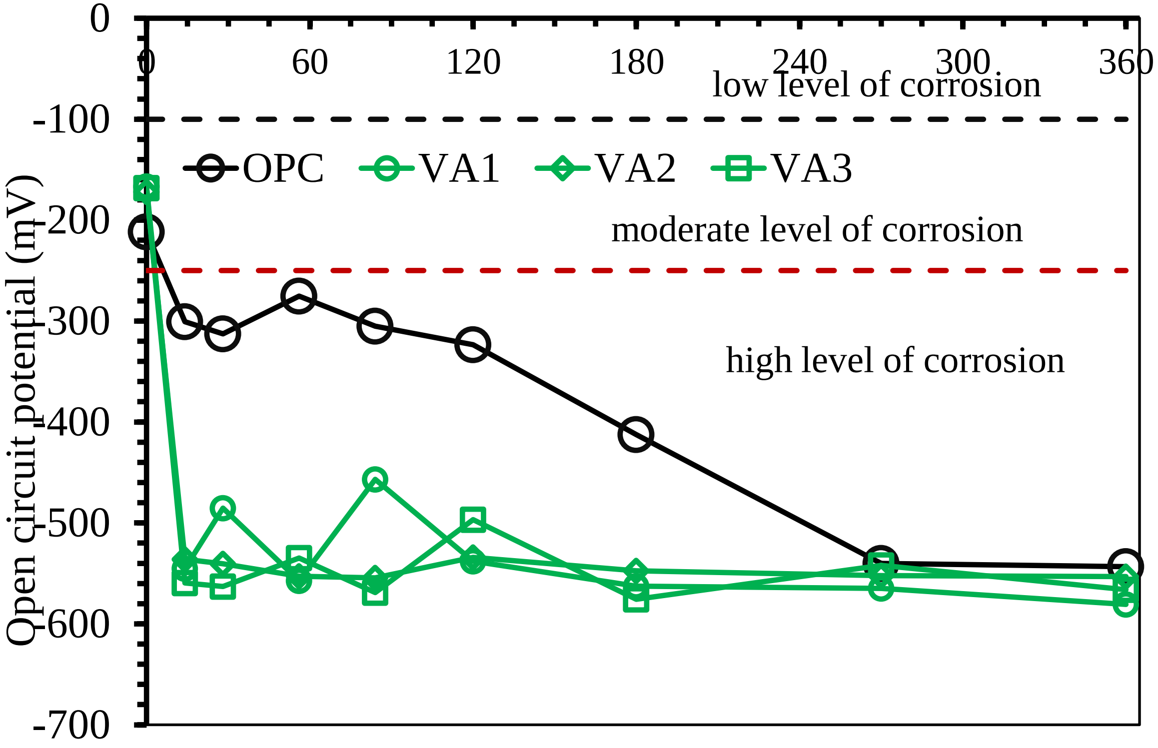
B = Tafel constant
β_a = Anodic Tafel constant, mV/decade
β_c = Cathodic Tafel constant, mV/decade
Rp= Polarization resistance, kΩ-cm^2



i_{corr} (μA/cm^2)	Classification
< 0.1	Passive/very low
0.1 to 0.5	Low/moderate
0.5 to 1.0	Moderate/high
> 1.0	Very High

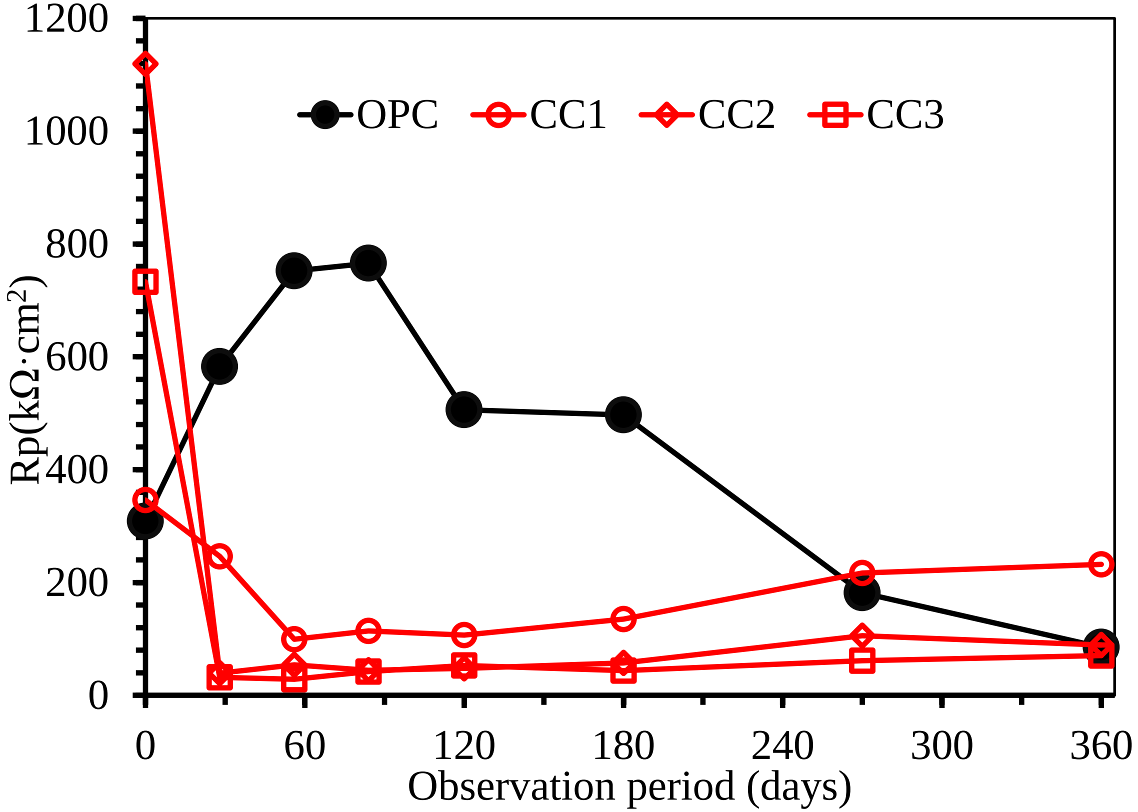
Open Circuit Potential (OCP)

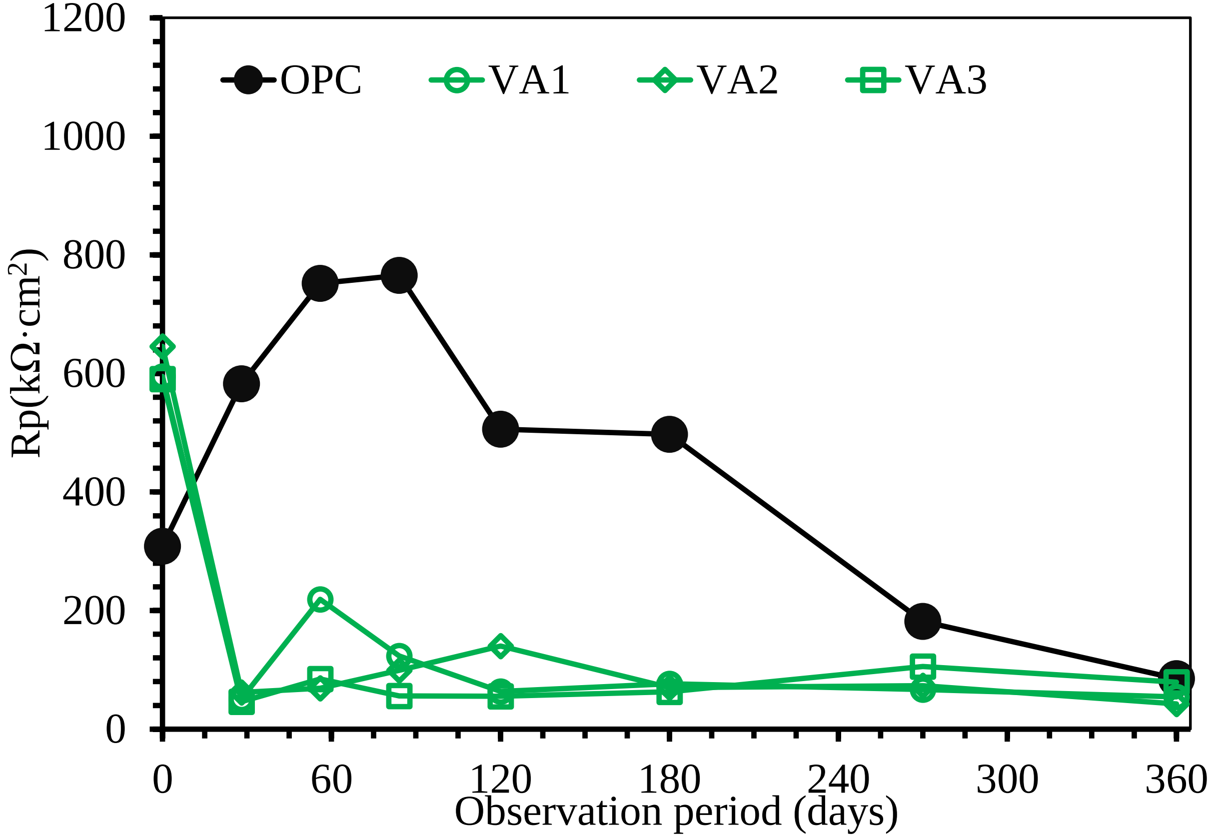




- Higher negative potentials observed for rebars embedded in AACs
- AAC's unique pore solution chemistry and lack of oxygen at the steel-concrete interface particularly at cathodic regions → refined microstructure

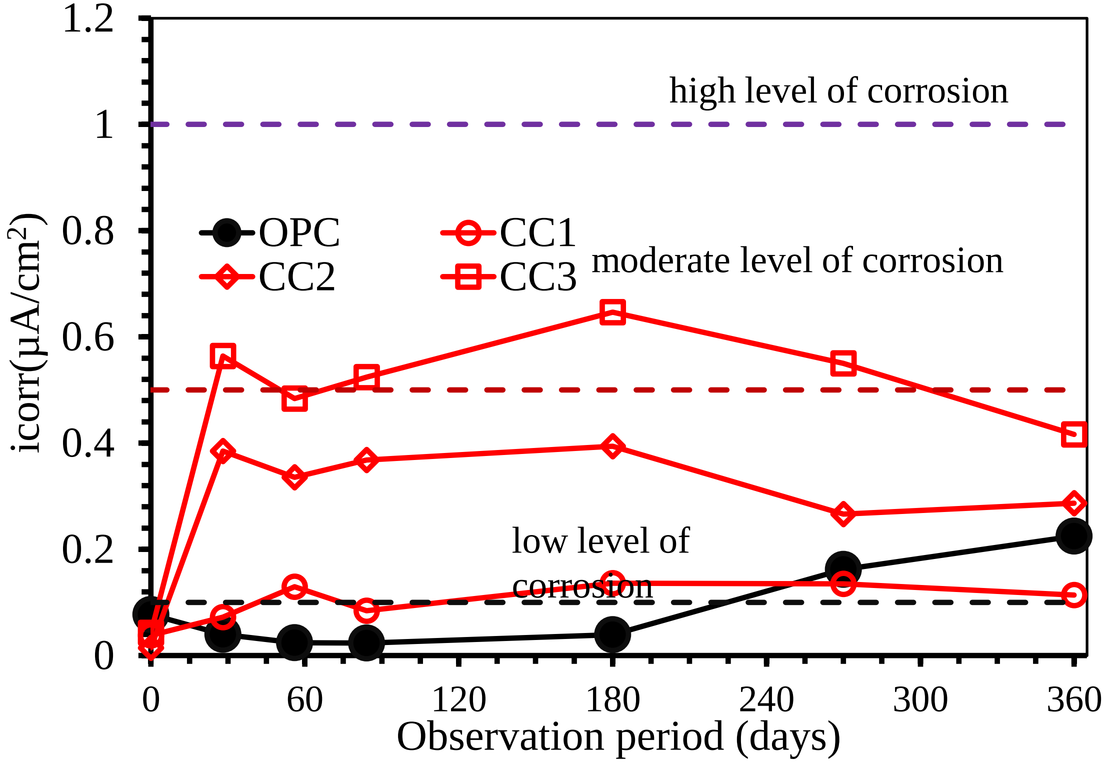
Linear Polarization Resistance (Rp)

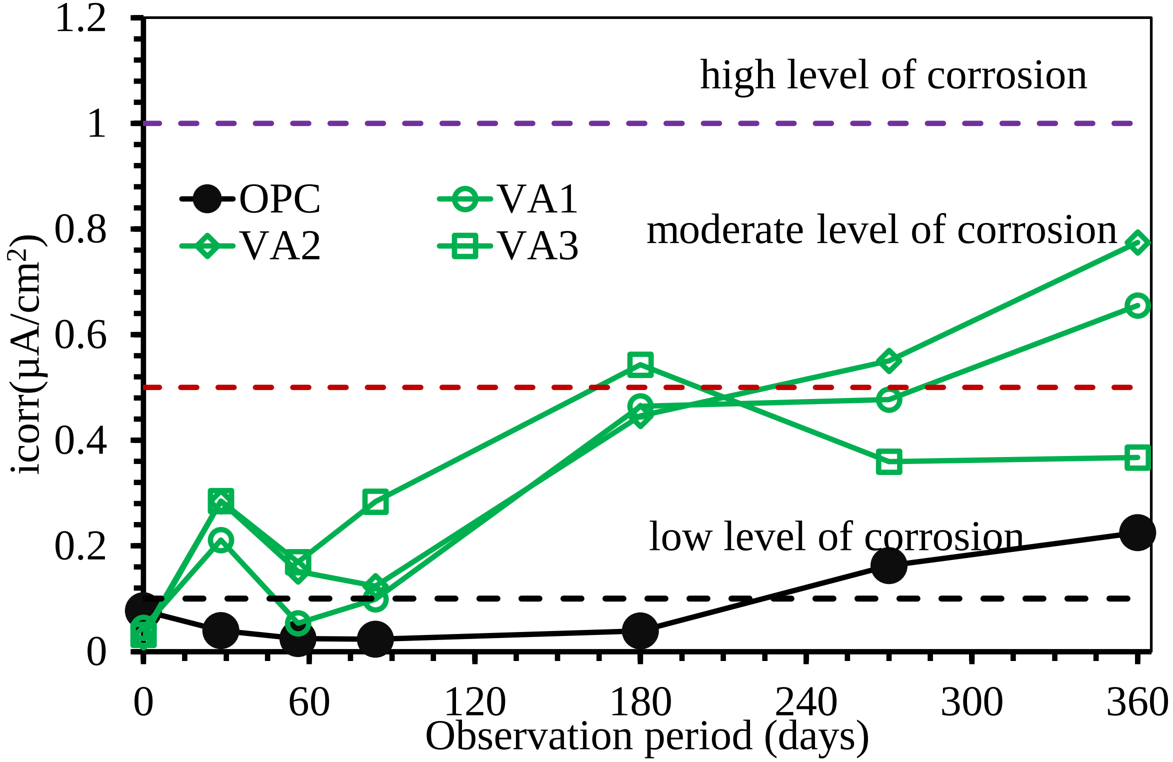




- A sharp decline followed by a stable trend is noted in Rp observation for reinforced AACs.
- Similar to corrosion potential trends.
- OPC – the constant decline in Rp indicates the onset of corrosion activity.

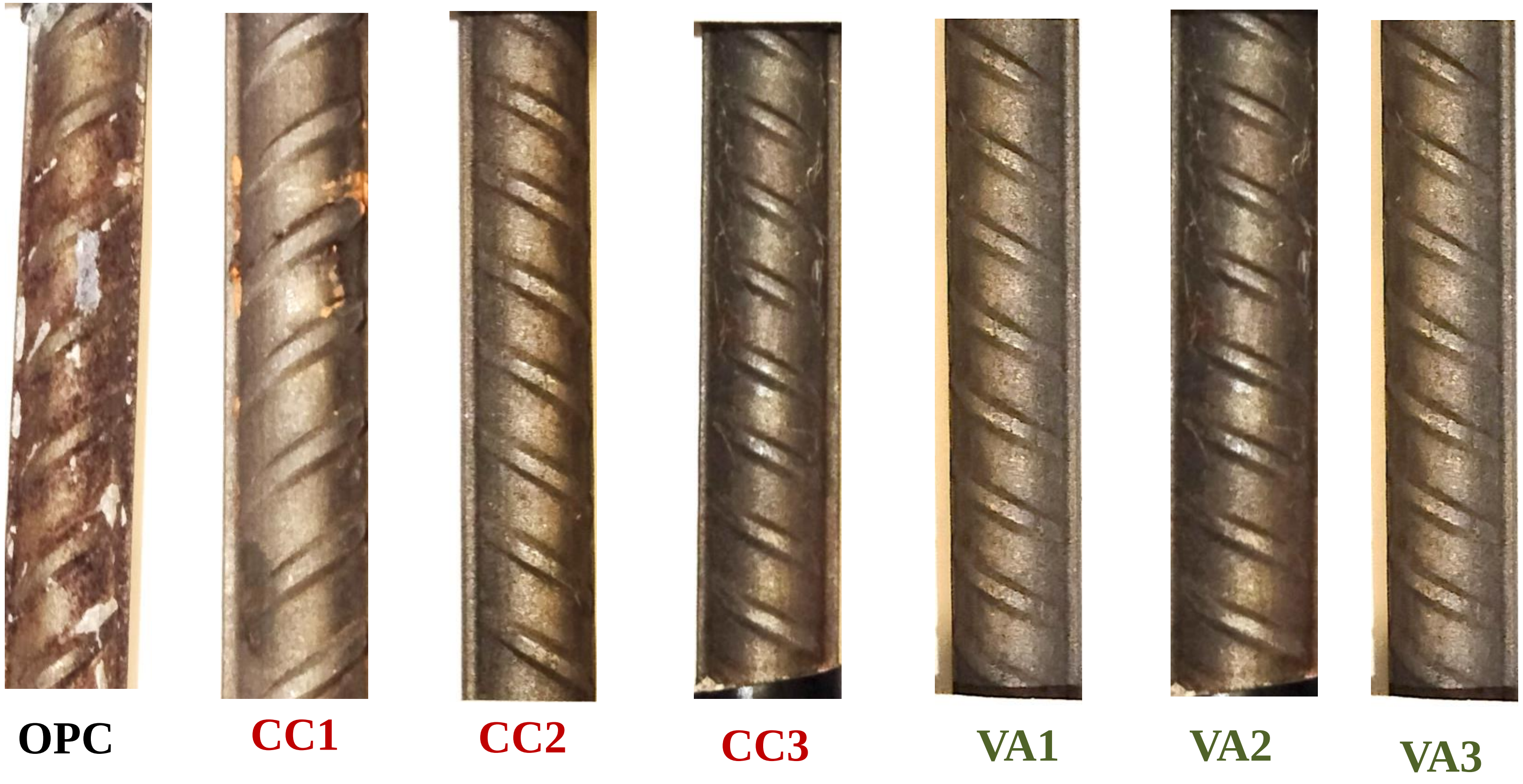
Corrosion Current Density (i_{corr})





- Higher apparent corrosion current densities for AACs -> potential depassivation of embedded rebars
- Indicates lower resistance of such AACs to chloride-initiated corrosion.

Retrieved reinforcements @ 1 year



- No signs of active corrosion/ rust stains/ pitting spots – noted for AACs.
- For OPC rebar: exposed area corroded

Tafel constants

Mixes	Tafel Constant (B) values in mV/decade							
	0 days	28 days	56 days	84 days	112 days	180 days	270 days	360 days
OPC	68.07	59.91	50.25	44.4	47	29.54	23.31	19.21
CC1	13.20	17.87	12.89	9.65	17.29	18.38	29.24	26.40
CC2	16.25	15.08	18.02	16.35	16.34	22.58	28.17	25.62
CC3	31.33	18.00	44.72	21.98	39.59	28.22	33.91	29.26
VA1	27.05	10.79	11.75	12.18	32.23	35.52	31.77	35.49
VA2	17.49	17.69	10.49	12.24	40.22	31.28	34.00	32.86
VA3	18.77	13.19	14.36	15.93	35.29	34.22	37.92	29.09

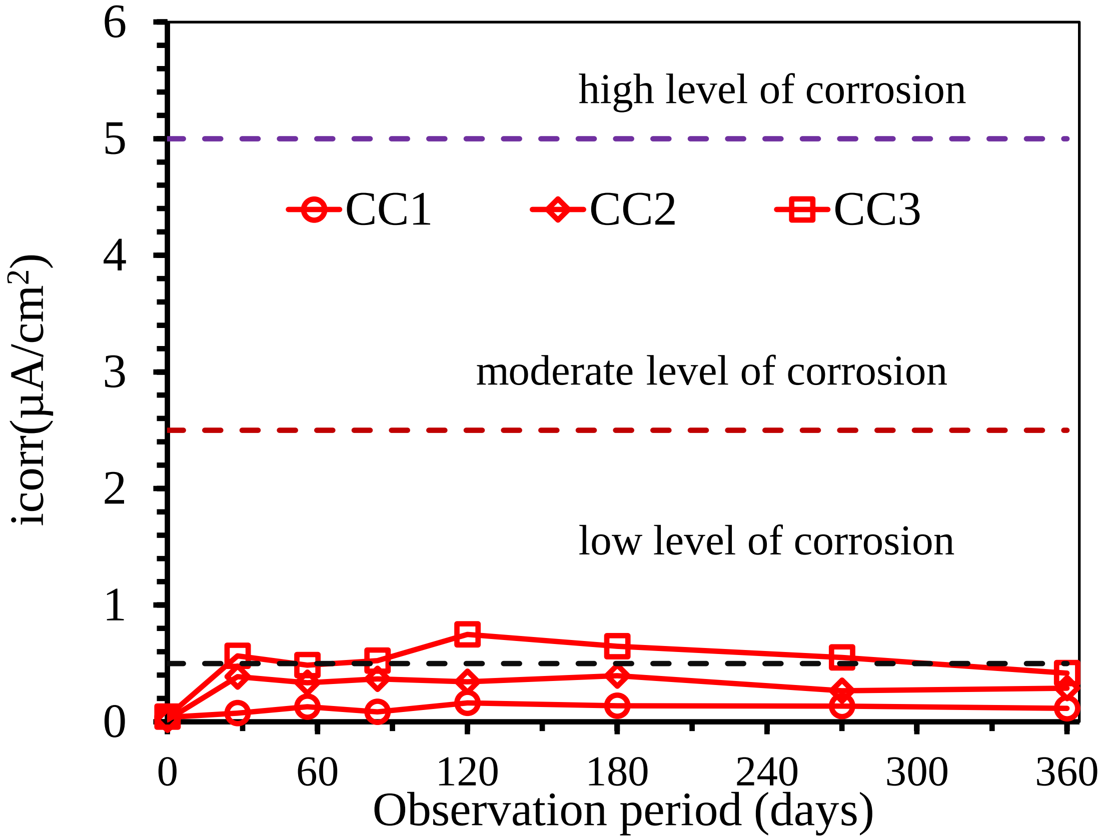
- Literature B for OPC: 26 (active) and 52(passive)
- AAC's vary b/w 10 to 35.
- Literature B values (13 to 25) for passive low calcium binder-based AACs Vs. 52 for OPC.
- OPC-centric thresholds are unfit to verify the corrosion activity in AACs.

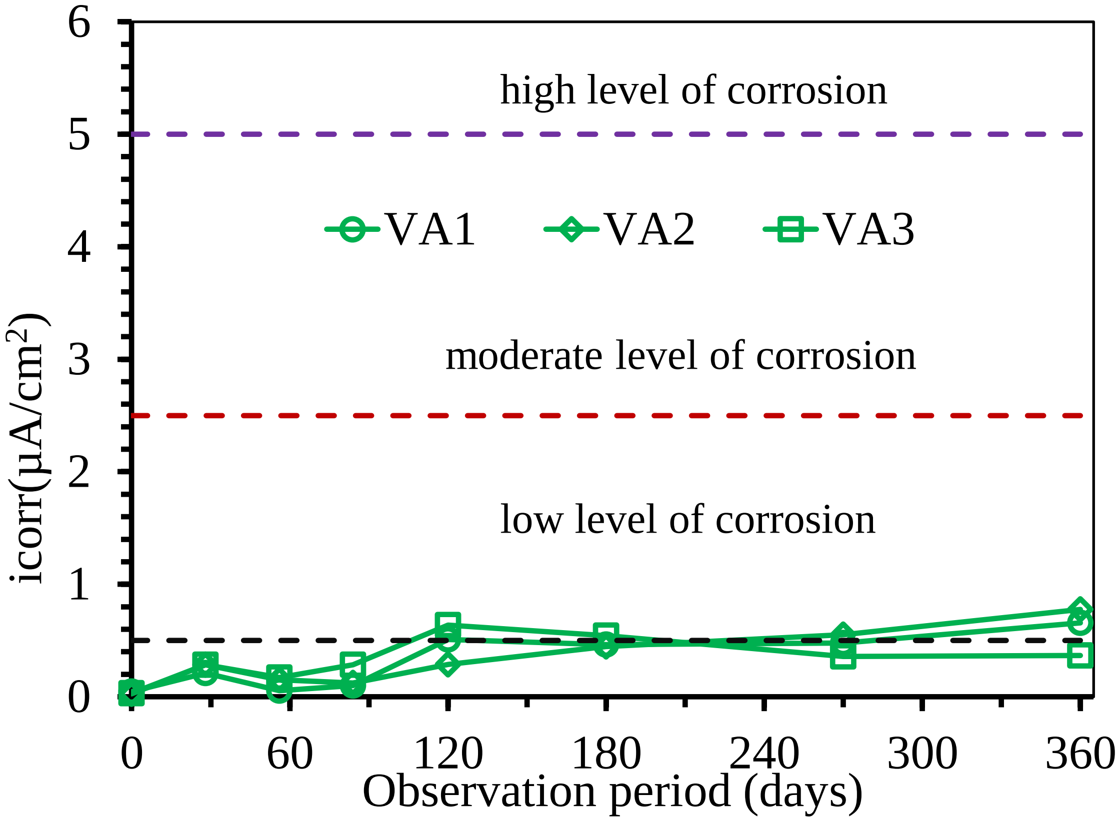
Icorr (μA/cm²)	Corrosion level
< 0.5	Negligible
0.5-2.5	Low
2.5-5	Moderate
>5	High

- Existing literature suggests a revision of the thresholds to increase by 3 to 5 times.

$$i_{corr} = \frac{B}{Rp}$$

Recommended Thresholds





Summary and Future Works

- All the tested AACs demonstrate significant resistance to chloride-induced corrosion.
- Distinction in corrosion response from conventional concrete – Unique pore solution composition
- OPC–specific standard limits were unfit to predict corrosion activity in studied AACs.
- Need to redesign the thresholds to accommodate the actual condition of rebars as confirmed by extractions.
- Revised limits indicate negligible to minor corrosion activity in AACs.

Future Works

- Correlating the pore solution chemistry of AACs to the corrosion characteristics
- Relating bulk chloride diffusion response of AACs to the corrosion behavior.

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