Supplementary Information

Fundamental Insights into the Stabilisation and Chemical Degradation of the Corrosion Product Scales

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Supplementary Methods

Various $Ca_{1-x}Fe_xCO_3$ are isostructural and share following d-spacing (d) equation for a Hexagonal bravais lattice：

$$\frac{1}{d^2} = \frac{4}{3}\left(\frac{(h^2 + hk + k^2)}{a^2}\right) + \frac{l^2}{c^2} \quad (1)$$

Where *h*, *k*, and *l* are the Miller Indices for (1 0 4) plane. The *a* and *c* values are unit cell parameters and relate to the Unit cell volume (V) for a hexagonal system:

$$V = a^2 * c * sin(60^o) \quad (2)$$

Substituting equation Supplementary (2) into equation Supplementary (1) gives the following relationsip:

$$\frac{1}{d^2} = \frac{4}{3}\left(\frac{(h^2 + hk + k^2)c\sqrt{3}}{2V}\right) + \frac{l^2}{c^2} \quad (3)$$

According to the linear relationship as follows [1]:

$$c = 1.6885x + 15.373 \quad (4)$$

$$V = 74.107x + 291.34 \quad (5)$$

Inserting Supplementary equations (4) and (5) into Supplementary equation (3) gives;

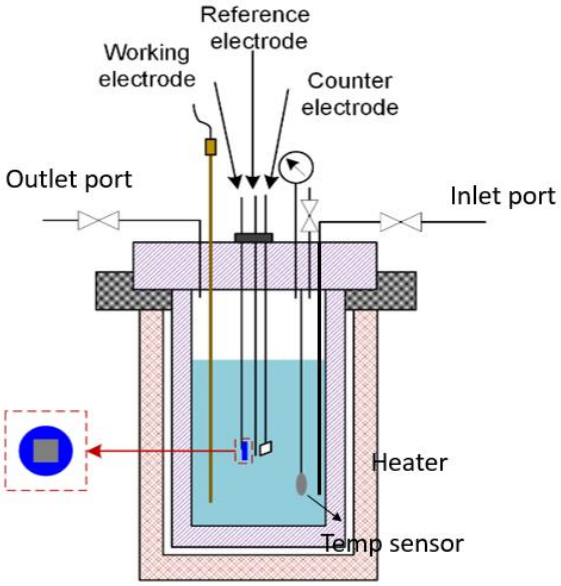
$$\frac{1}{d^2} = \frac{4}{3}\left(\frac{(h^2 + hk + k^2) * (1.6885x + 15.373) * \sqrt{3}}{2 * 74.107x + 291.34}\right) + \frac{l^2}{(1.6885x + 15.373)^2} \quad (6)$$

The (1 0 4) plane for x=0 and x=1 are located at 2theta 29.42 and 32.07 respectively which gives the relationship between d (1 0 4) and calcium proportion x in $Ca_{1-x}Fe_xCO_3$:

$$\frac{1}{d^2} = \frac{4}{3}\left(\frac{2.92456x + 26.62681}{148.214x + 582.68}\right) + \frac{16}{(1.6885x + 15.373)^2} \quad (7)$$

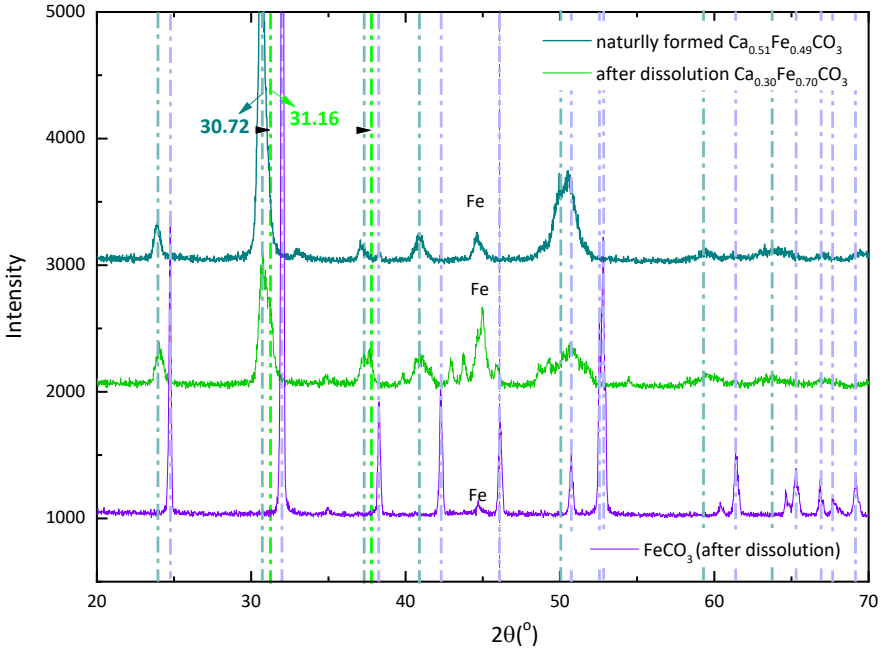
Supplementary Figures

Supplementary Figure 1. A schematic diagram



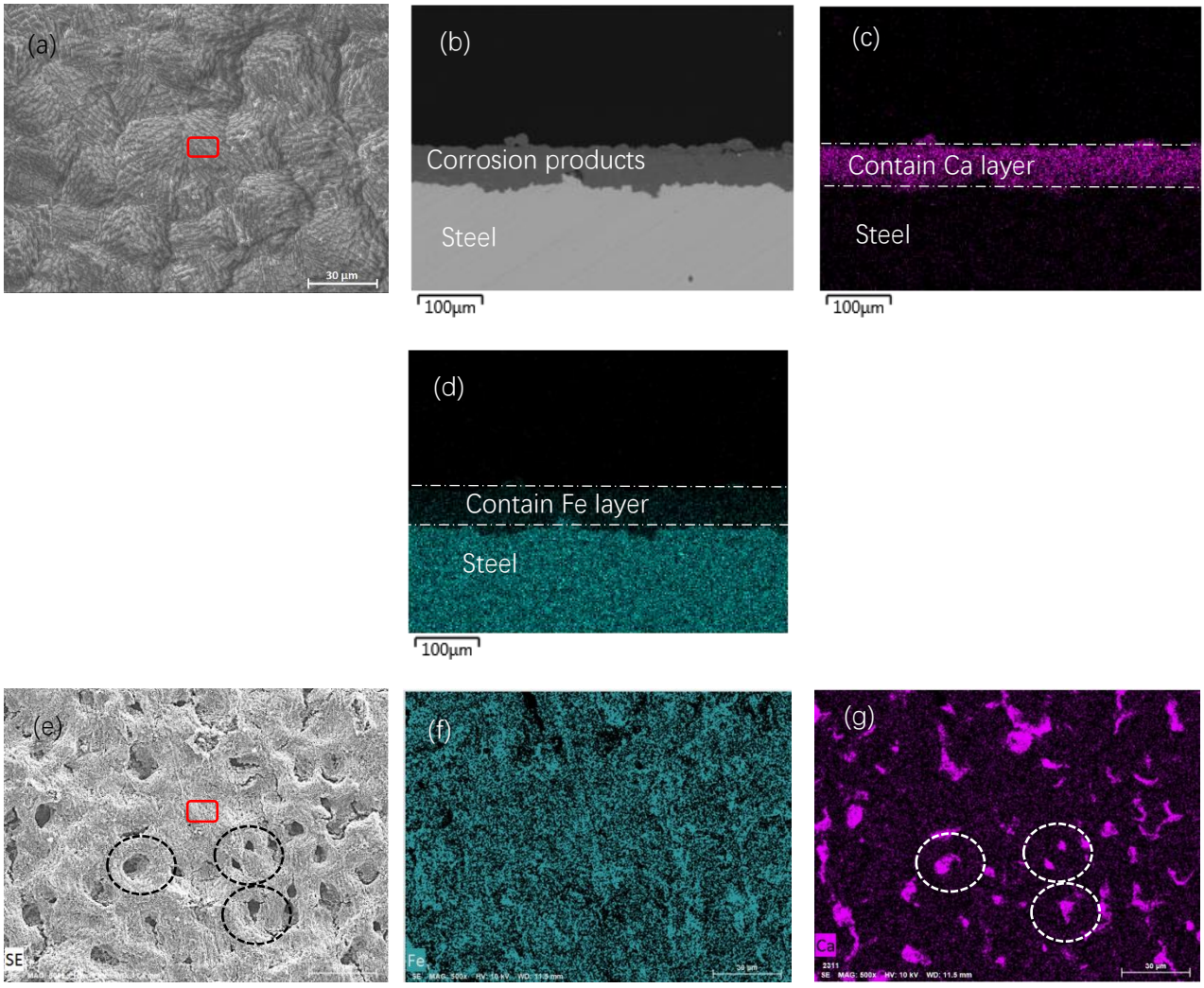
A schematic diagram of an in-situ electrochemical autoclave for the formation and dissolution experiments.

Supplementary Figure 2. Composition of the corrosion scales



XRD patterns of the corrosion scales before and after the dissolution experiments formed on the surface.

Supplementary Figure 3. Surface morphology and composition of the corrosion scales at the interface

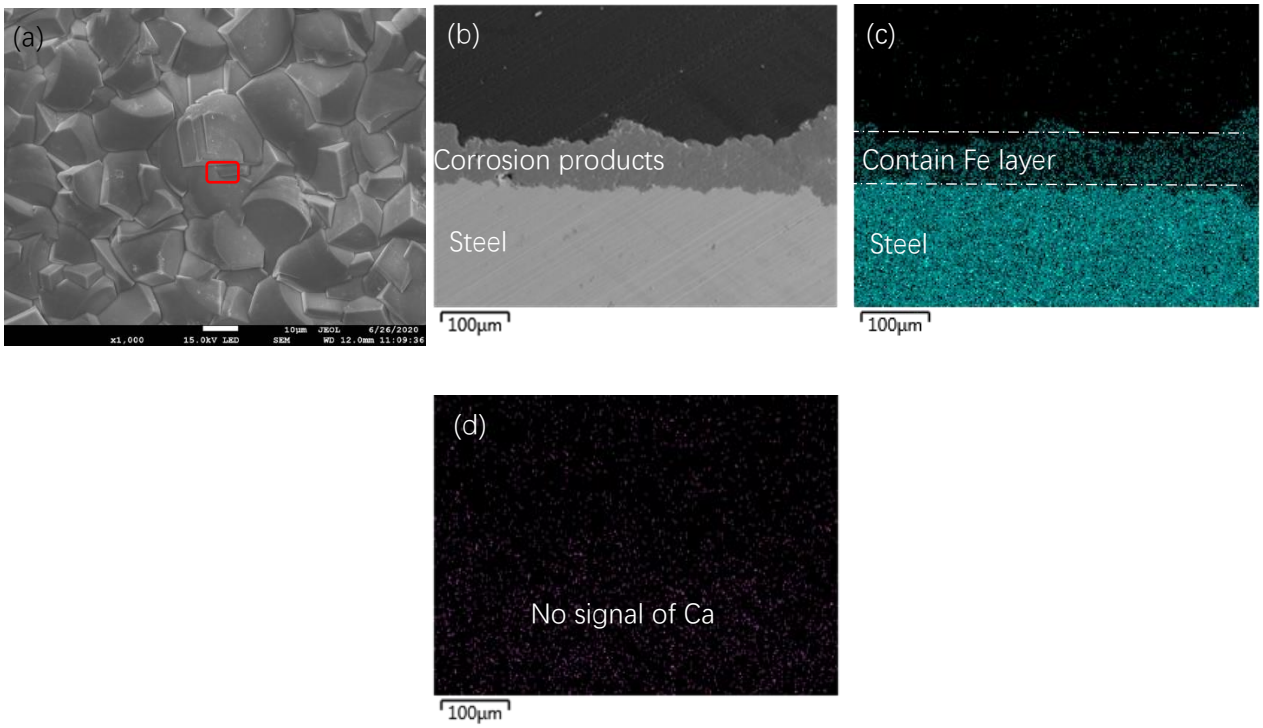


(h)

Atom (%)	Fe	Ca
(a-c) Before dissolution	56.27	43.73
(d-f) After dissolution	96.47	3.53

The morpholigy and compsotion of (a-d) $Ca_{0.51}Fe_{0.49}CO_3$ scales before dissolution experiments, (e-g) $Ca_{0.51}Fe_{0.49}CO_3$ scales after dissolution experiments and (h) the composition comparisons (labelled as red box in (a) and (e)) before/after the dissolution experiments.

Supplementary Figure 4. Surface morphology and composition of FeCO3 formed on the surface



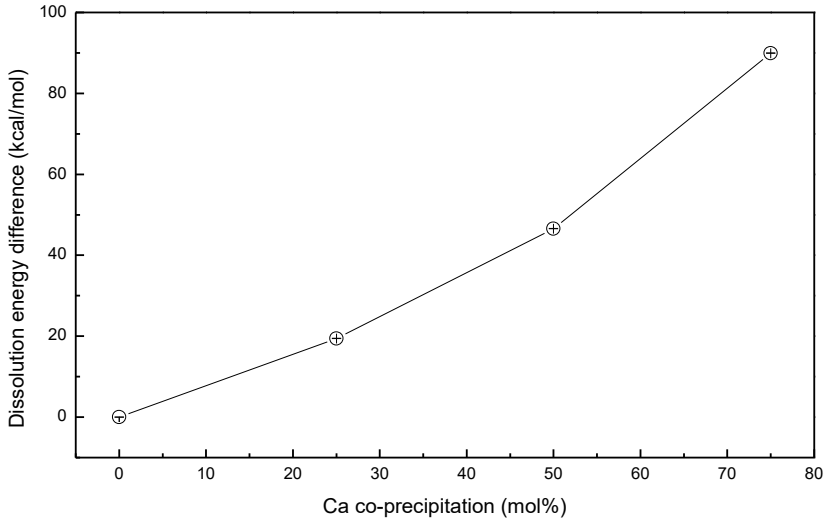
The surface morphology and cross-section images of the naturally formed $FeCO_3$ scales before dissolution experiments on the surface.

The required extra energy for losing Fe than losing Ca within various carbonates is expressed as follows:

$$E_{extra} = \left(E_{Ca_{1-x}Fe_xCO_{3(Fe-vac)}} - E_{Ca_{1-x}Fe_xCO_3}\right) - \left(E_{Ca_{1-x}Fe_xCO_{3(Ca-vac)}} - E_{Ca_{1-x}Fe_xCO_3}\right) \quad (8)$$

$$= E_{Ca_{1-x}Fe_xCO_{3(Fe-vac)}} - E_{Ca_{1-x}Fe_xCO_{3(Ca-vac)}}$$

Supplementary Figure 5. The calcualtion of the extra energy



The calcualtion of extra energy to lose Fe than losing Ca within various Fe-Ca mixed carbonates.