Protection of marine structures from ALWC by calcareous deposits

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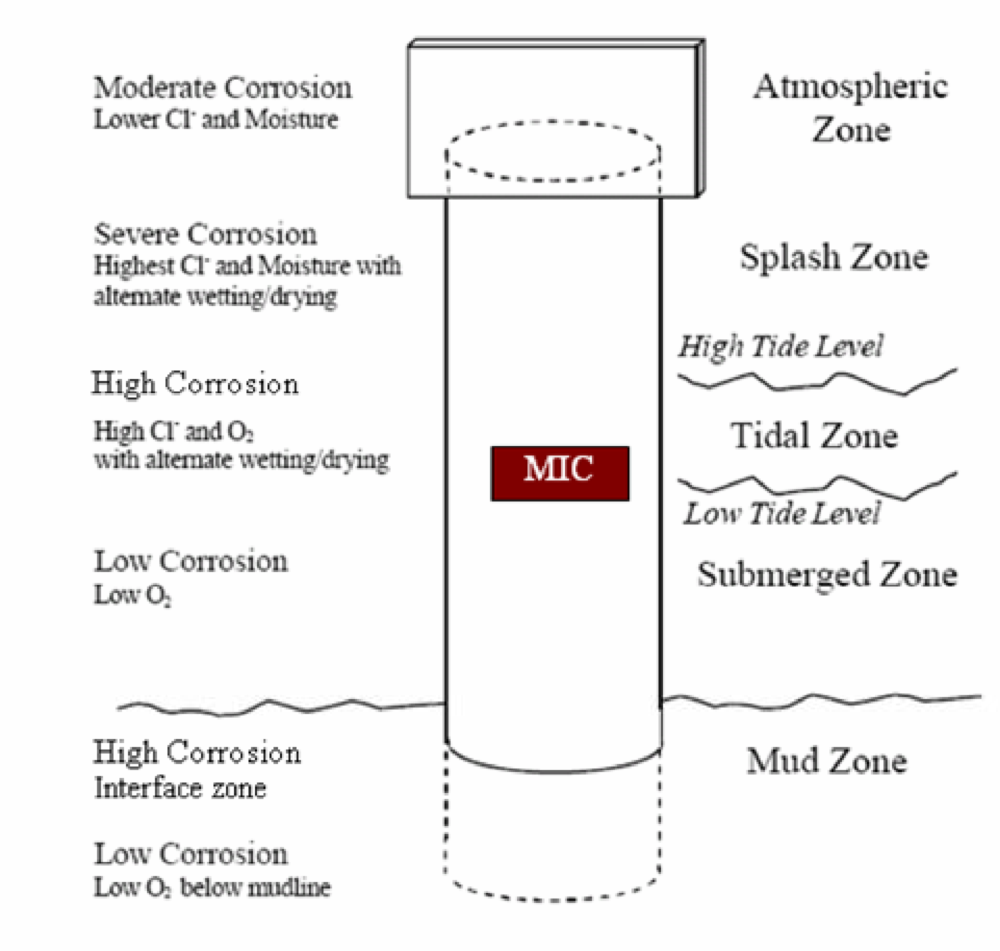
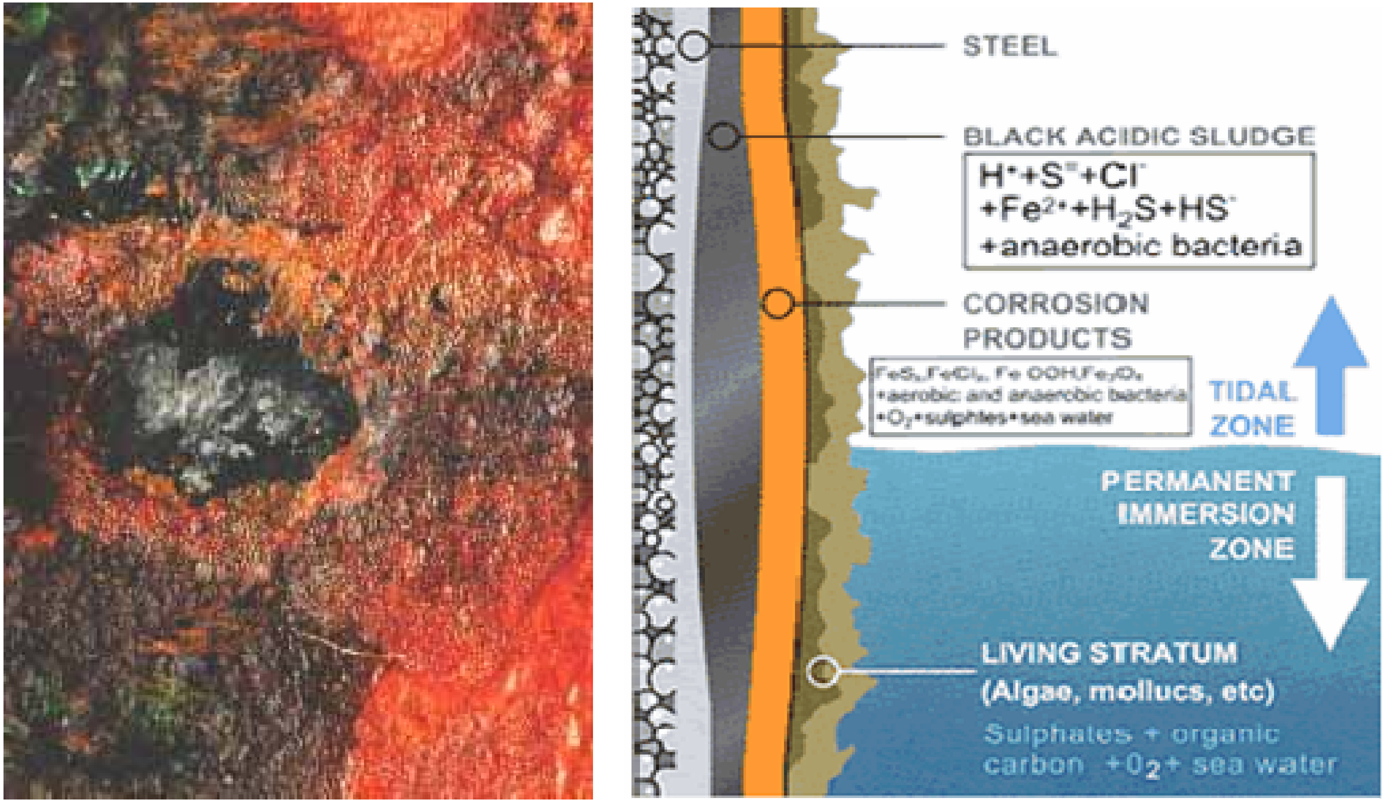


Corrosion level and positions over the length of steel pile in seawater

Source: American Society of Civil Engineers (ASCE)

Accelerated Low Water Corrosion

- ☐ First identified in the early 1960s
- ☐ Recognition of ALWC patches
  - Poorly adherent
  - Bright orange of oxides of Fe and black of iron sulfide (FeS)
  - Clean, shiny and pitted steel surface
- ☐ Low water corrosion
- ☐ MIC: Microbiologically Influenced Corrosion
- ☐ Localised corrosion
- ☐ Just above the Lowest Astronomical Tide (LAT)
- ☐ Typical corrosion rates: 0.3-1.0 mm/wetted side/year



a

b

ALWC patches

Source: BAC (a) & Atlas Marine Contractors Limited (b)

Damage to steel structures due to ALWC

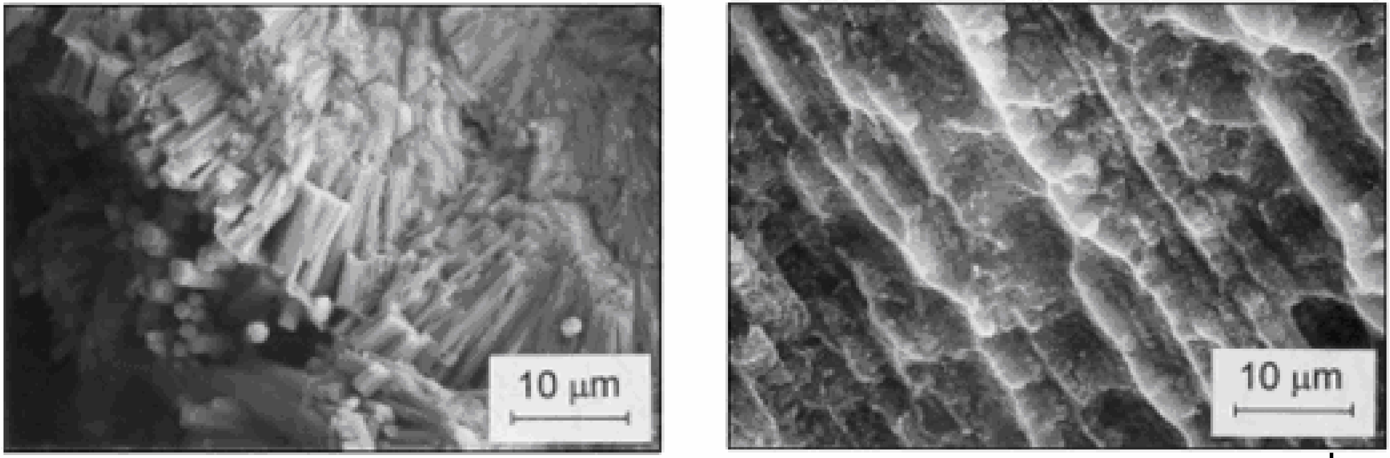
- ☐ Rapid and local metal thinning (corrosion rates can be up to 2 mm/wetted side/year)
- ☐ Loss of stability and strength of structures (serious holing)
- ☐ Premature structural failure leads to
  - Partial or complete reconstruction of a structure
  - Total shutdown of a system

LATreat Method

1. Corrosion product cleaning
    - $2H_2O + 2e^- \rightarrow 2OH^- + H_2\uparrow$
2. Microorganism sterilisation
    - Relatively high anodic current
    - $2Cl^- \rightarrow Cl_2\uparrow + 2e^-$
3. Cathodic polarisation - increases alkalinity at the metal surface, causes deposition of calcareous film
    - $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$
    - $HCO_3^- + OH^- \leftrightarrow H_2O + CO_3^{2-}$
    - $Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3\downarrow$
    - $Mg^{2+} + 2OH^- \rightarrow Mg(OH)_2\downarrow$

Calcareous deposit

- $CaCO_3$:
  - Calcite (more stable)
  - Aragonite (more compact, majority in deposit)
- $Mg(OH)_2$: Brucite
- Magnesium ions limit the nucleation and growth of calcite but only slow the nucleation of aragonite



a

b

Typical morphology of aragonite (a) and brucite (b)
(Source: Salvago, G & Bollini, G.)

A typical calcareous deposit formed in artificial seawater in the laboratory

The experimental installation

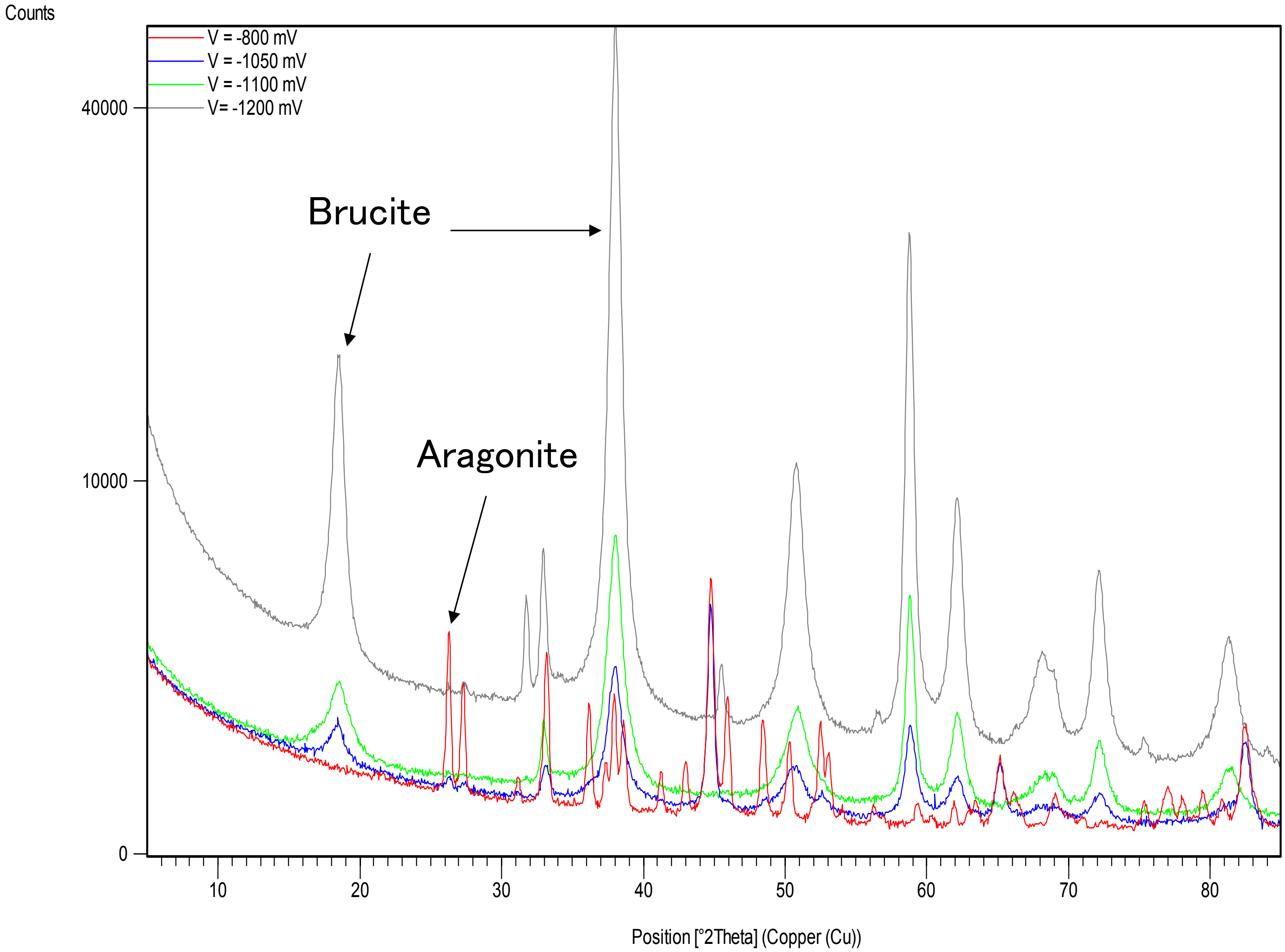
Experimental conditions

- ☐ Polarisation potentials -800 mV to -1300 mV (SCE)
- ☐ Air injection
  - Stirring to prevent local reaction
  - Simulation of sea condition
- ☐ Analysis methods
  - Scanning electron microscopy (SEM)
  - Energy Dispersive Analysis of X-rays (EDX)
  - X-ray diffraction (XRD)
  - Chemical analysis

Composition of calcareous films

Summary of XRD Spectra

- Major peaks in XRD analysis
  - Iron: 44.5° , 82° and 65°
  - Brucite: 38° and 18.5°
  - Aragonite: 26° , 27° , 46° and 33° (low-high double peak), minor peak at 21° also used as confirmatory indication
  - Calcite: 29.5° , 31.5° and 23°
  - (Major peaks indicated in blue)

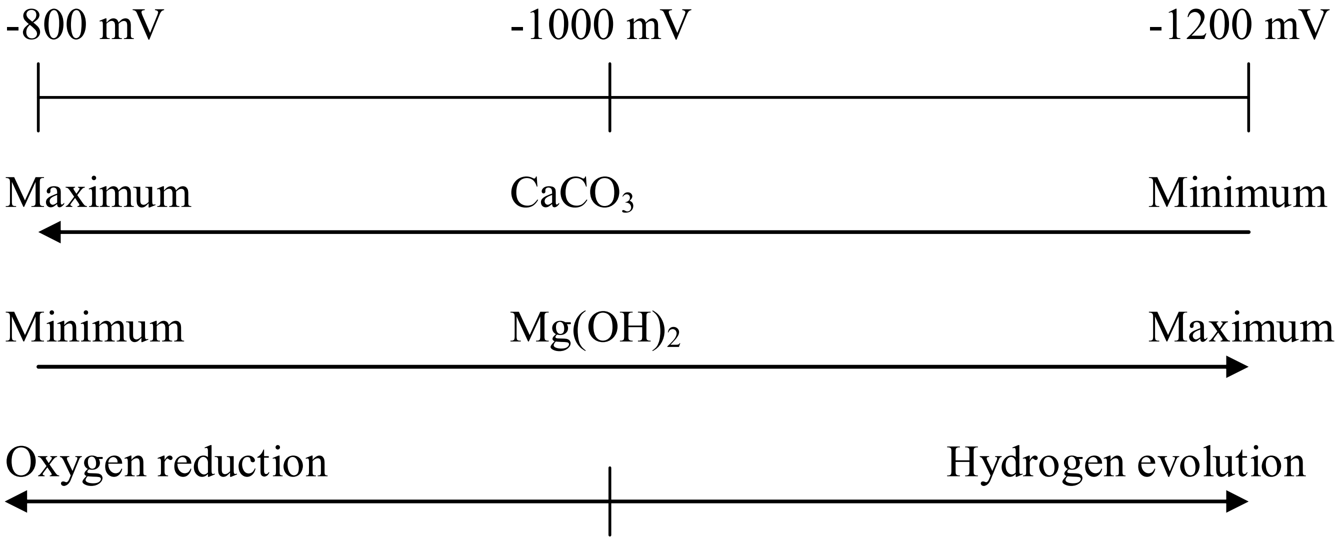


XRD curves of calcareous films at -800, -1050, -1100 and -1200 mV

Possible precipitates vs. pH at metal surface

Precipitate	***pH***	***Note***
Brucite	≥ 9.25	More negative potentials
Calcite	≥ 7.75	
Aragonite	≥ 8.00	

Trend of calcareous film formation in artificial seawater



-800 mV | -1000 mV | -1200 mV

Maximum ← $CaCO_3$ ← Minimum

Minimum → $Mg(OH)_2$ → Maximum

Oxygen reduction ← | → Hydrogen evolution

Initial results

- ☐ E < -1000 mV: Hydrogen evolution is predominant
  - Advantages: faster deposition/thicker deposits
  - Disadvantages: coating defects + high porosity
- ☐ E ≥ -1000 mV: Oxygen reduction is predominant
  - Advantages: high adherence + fewer coating defects
  - Disadvantages: thin calcareous film
- ☐ Calcite not detected at any potential, $CaCO_3$ only present as aragonite

Components of calcareous deposit according to potentials - DC deposition

Polarisation potential (mV)	**Aragonite**	**Calcite**	**Brucite**	**Predominant reaction**
-800	Major	-	-	Oxygen reduction
-1050	Minor	-	Major	Moderate hydrogen evolution
-1100	Trace	-	Major	Aggressive hydrogen evolution
-1200	Trace	-	Major	Aggressive hydrogen evolution

Future Study

- Evaluate corrosion rate (Electrochemical Impedance) of steel with and without deposit and as a function of deposit properties.
- Develop methods to assess endurance of coating:
  - Erosion/wear e.g. using flowing seawater
  - Adherence and porosity (base on standards for adhesion of concrete to metal?)

Acknowledgements

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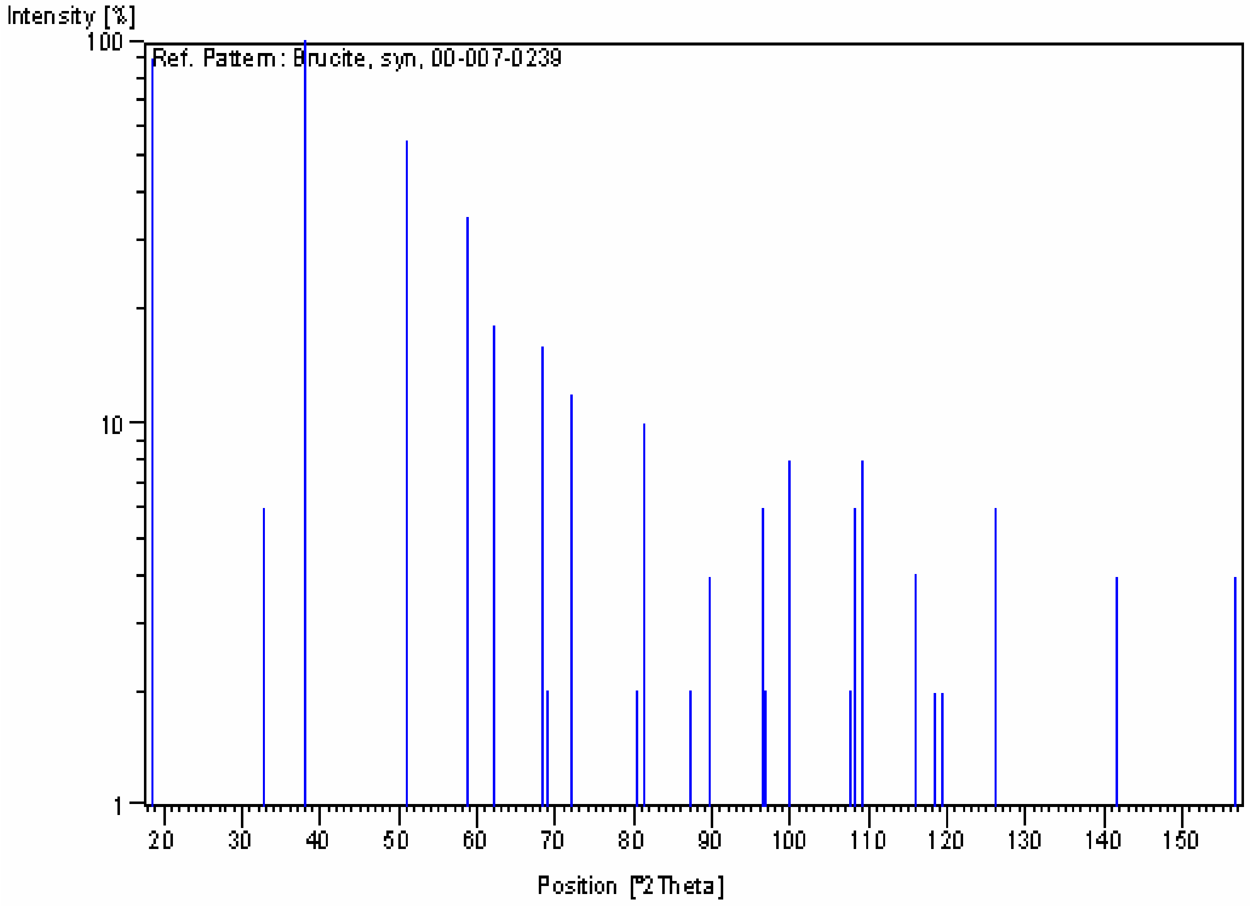
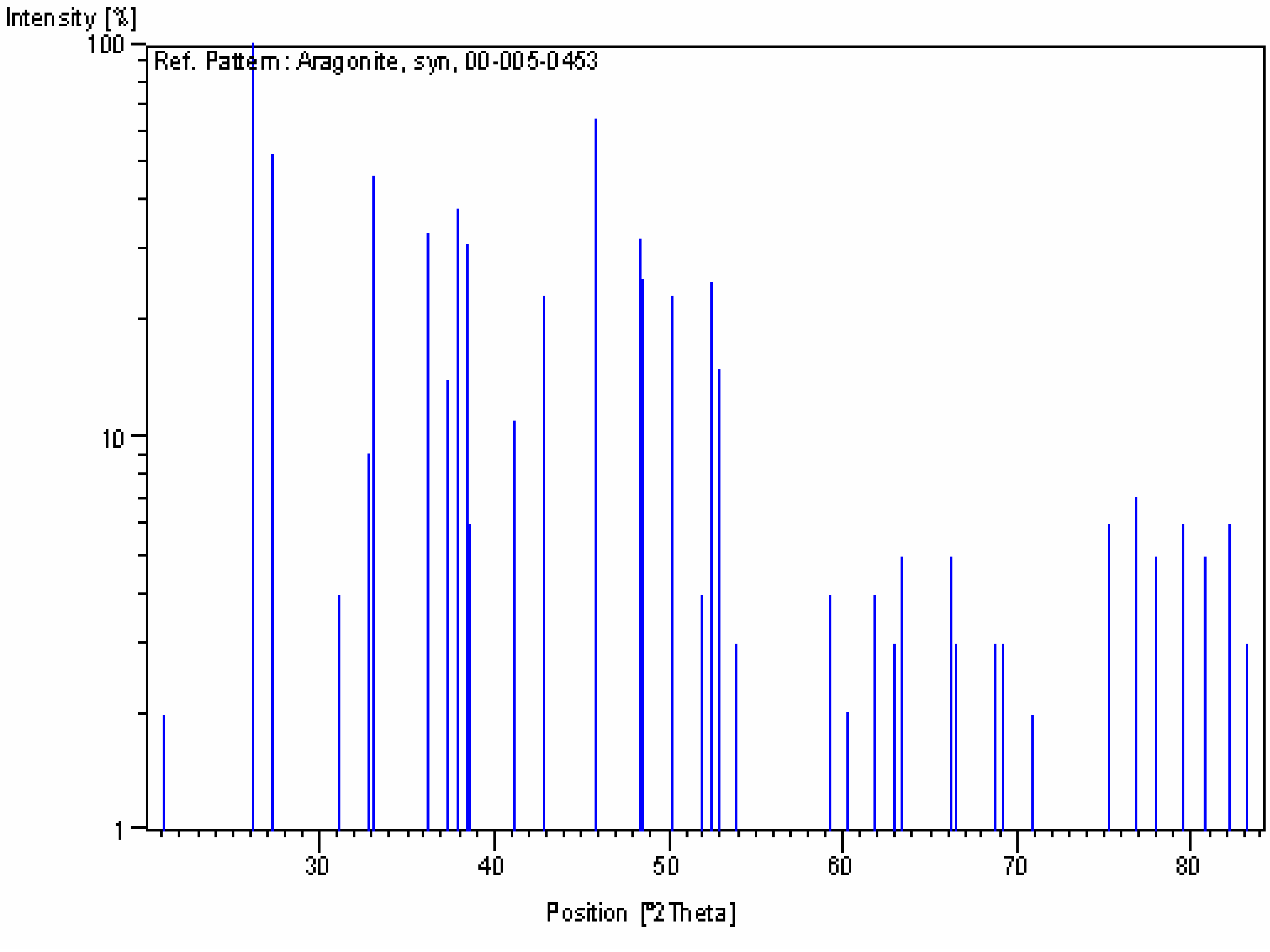
THANK YOU

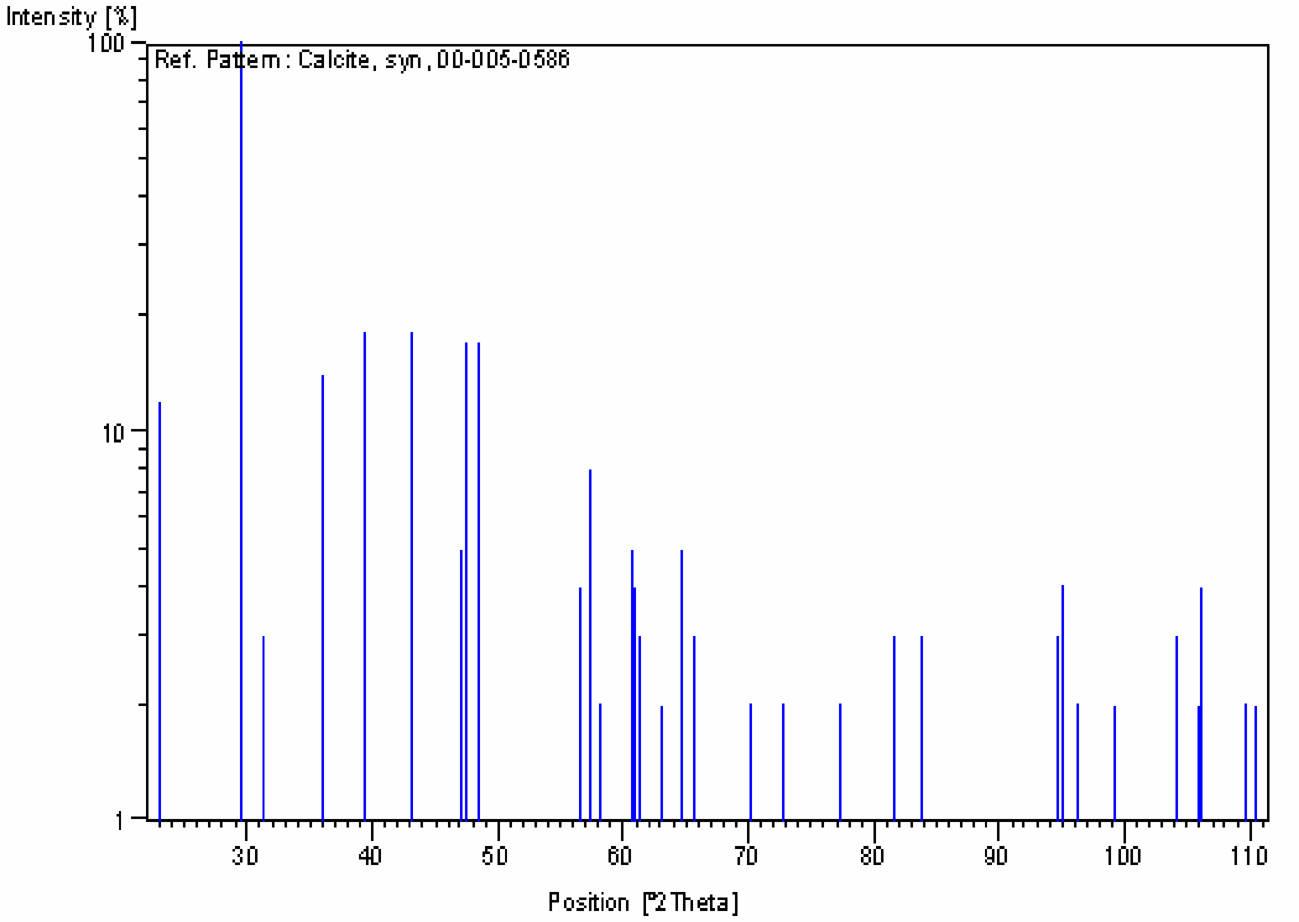
XRD Data for Reference



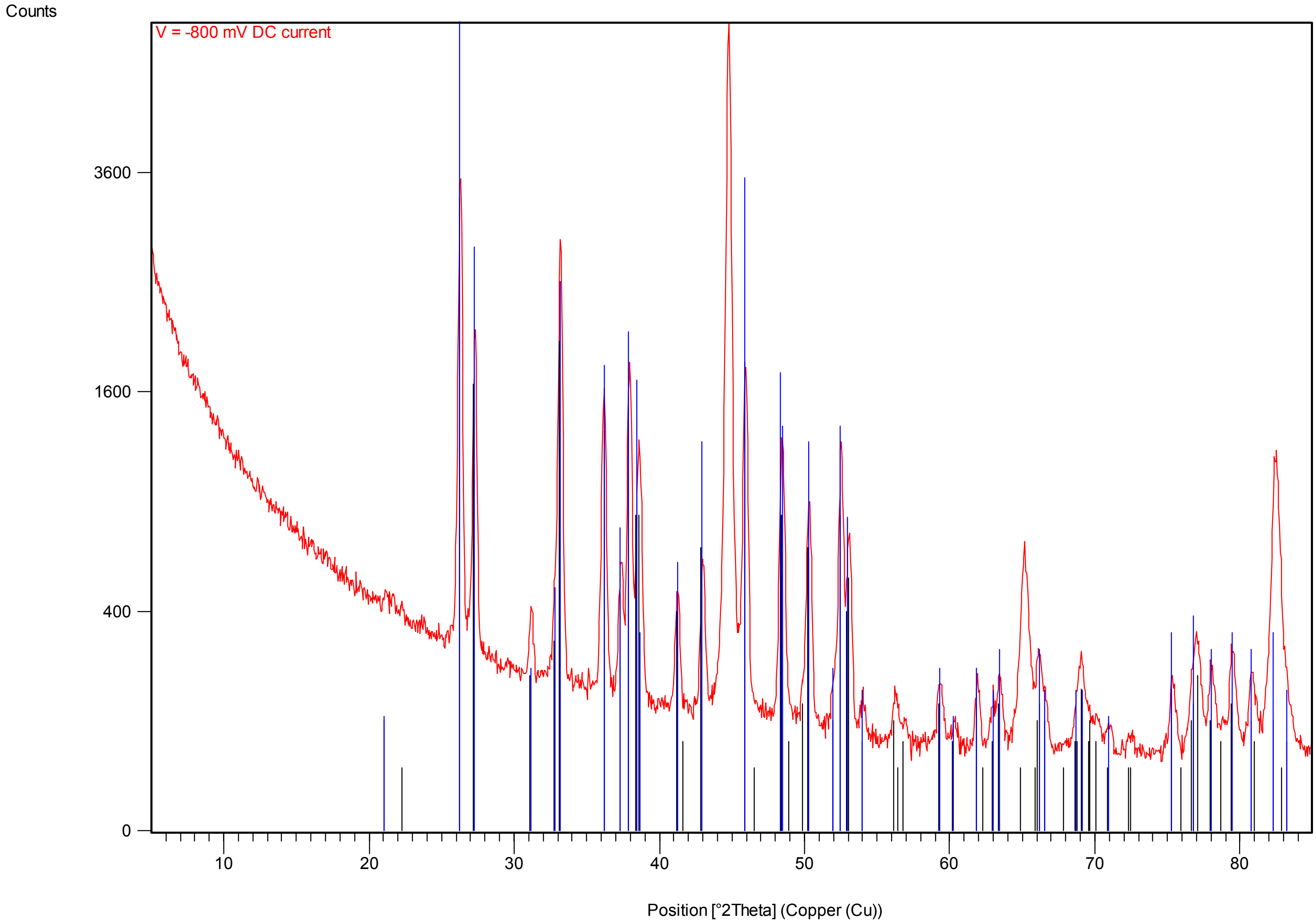
XRD standard for Brucite



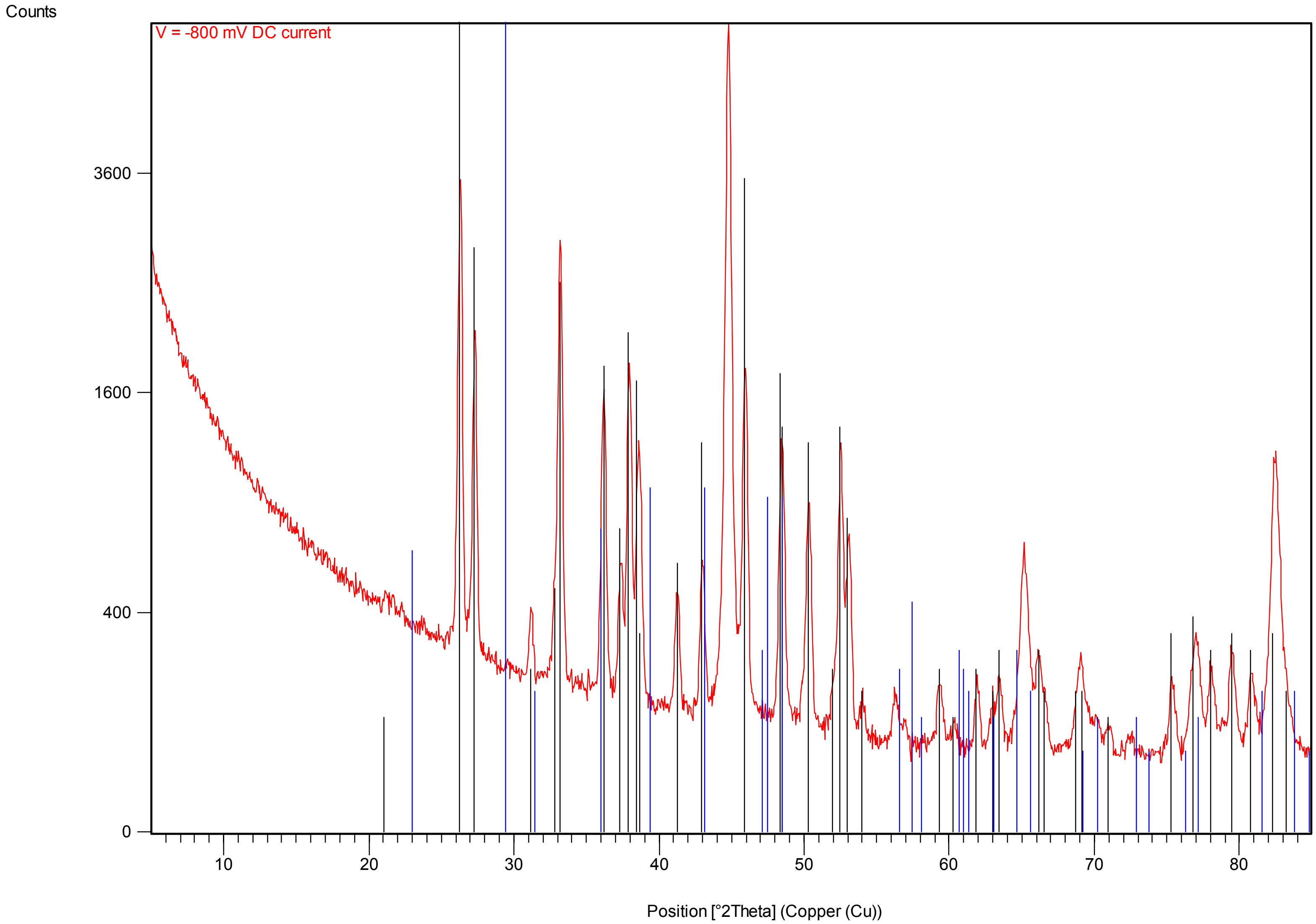
XRD standard for Aragonite



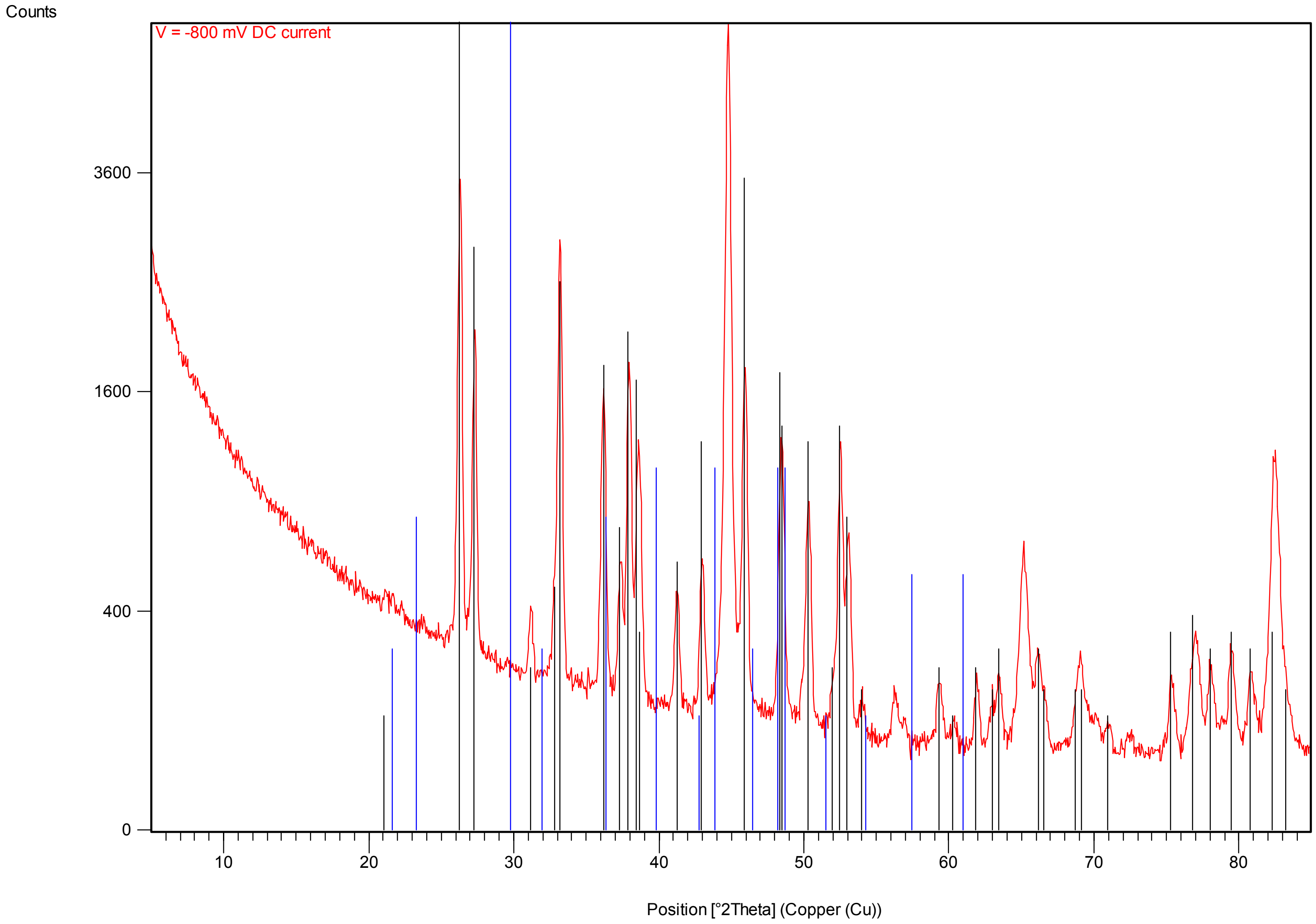
XRD standard for Calcite



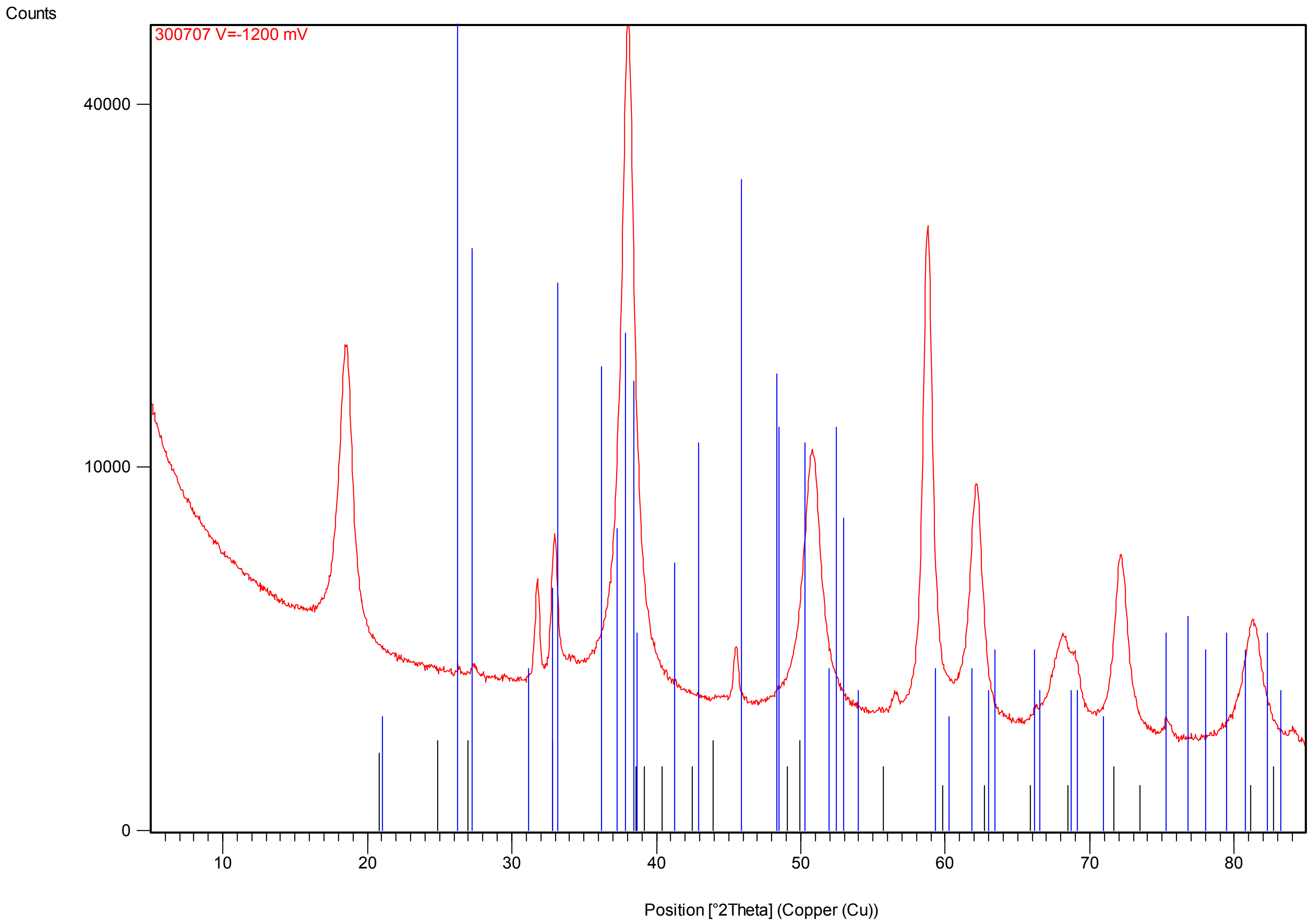
XRD curves of Calcareous Film (red) at -800 mV (Aragonite standard in blue)



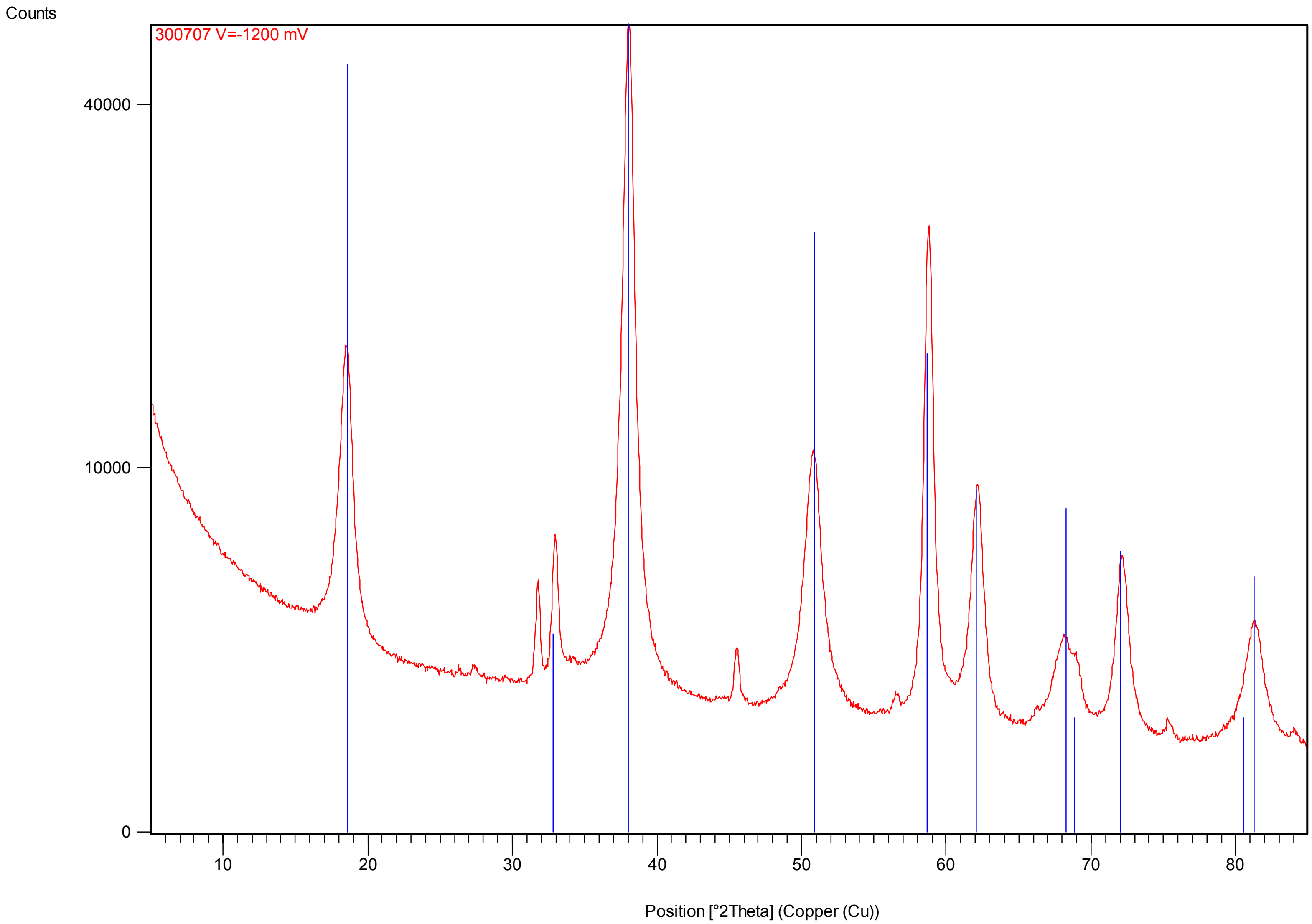
XRD curves of Calcareous Film (red) at -800 mV (Calcite standard in blue)



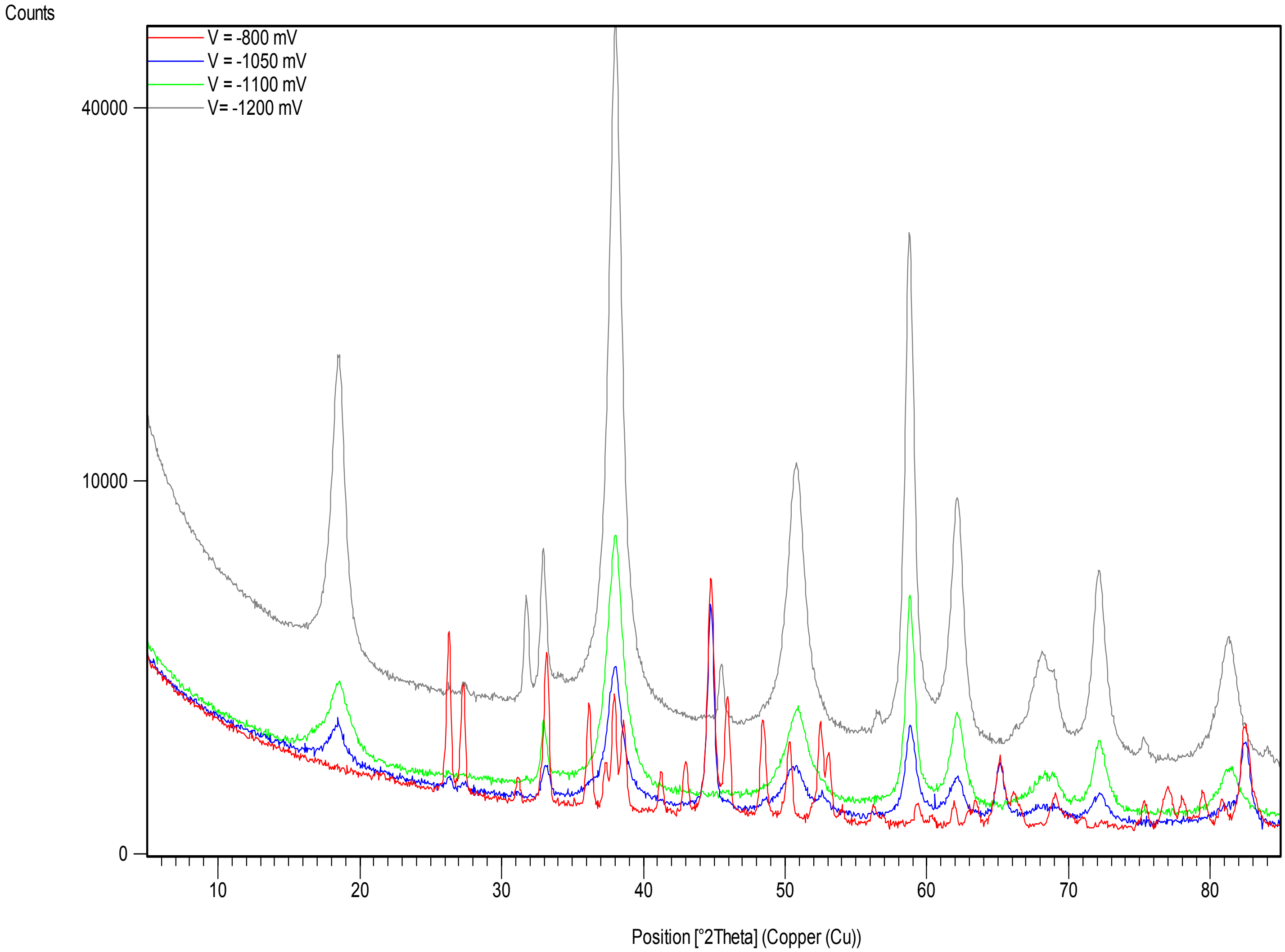
XRD curves of Calcareous Film (red) at -800 mV (Brucite standard in blue)



XRD curves of Calcareous Film (red) at -1200 mV (Aragonite standard in blue)



XRD curves of Calcareous Film (red) at -1200 mV
(Brucite standard in blue)



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