Neutralizing Amine Use in ACC Plants for pH Control

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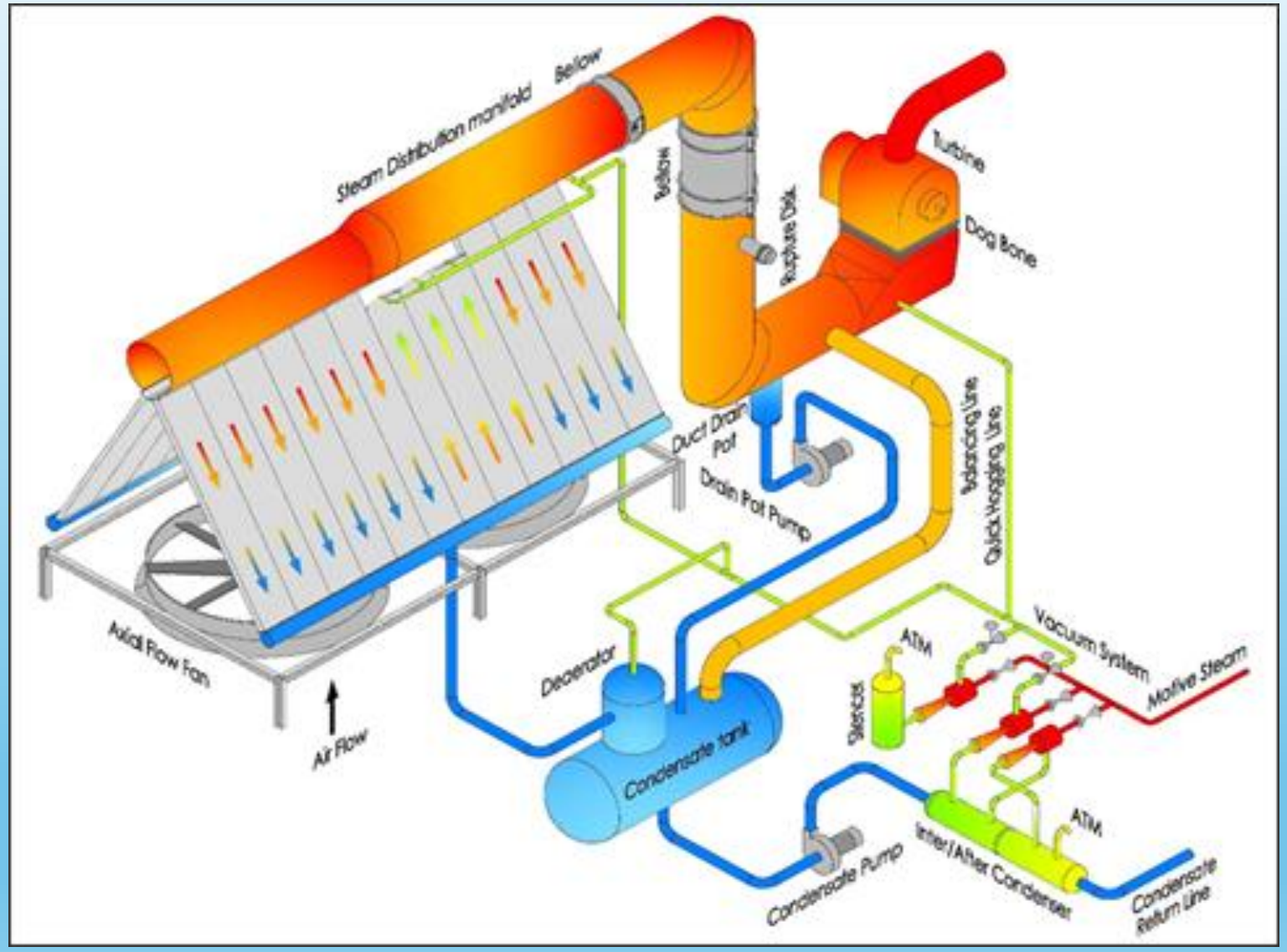
Neutralizing amines vs. ammonia for pH control

- Theoretical: amine elevates pH in droplets of early condensate
- Practical: influence of decomposition acidity
- Cost: favors ammonia (drains can be returned to the steam cycle)
- Feed management: favors ammonia (simplicity)
- ACC corrosion: can favor amine at a given pH if feed control is managed based on decomposition measurement
- Polisher resin:
  - high pH operation with ammonia reduces polisher effectiveness
  - amines can cause anion resin capacity loss

Forced Draft ACC diagram



Source https://www.evapco-blct.com/dry-cooling-101

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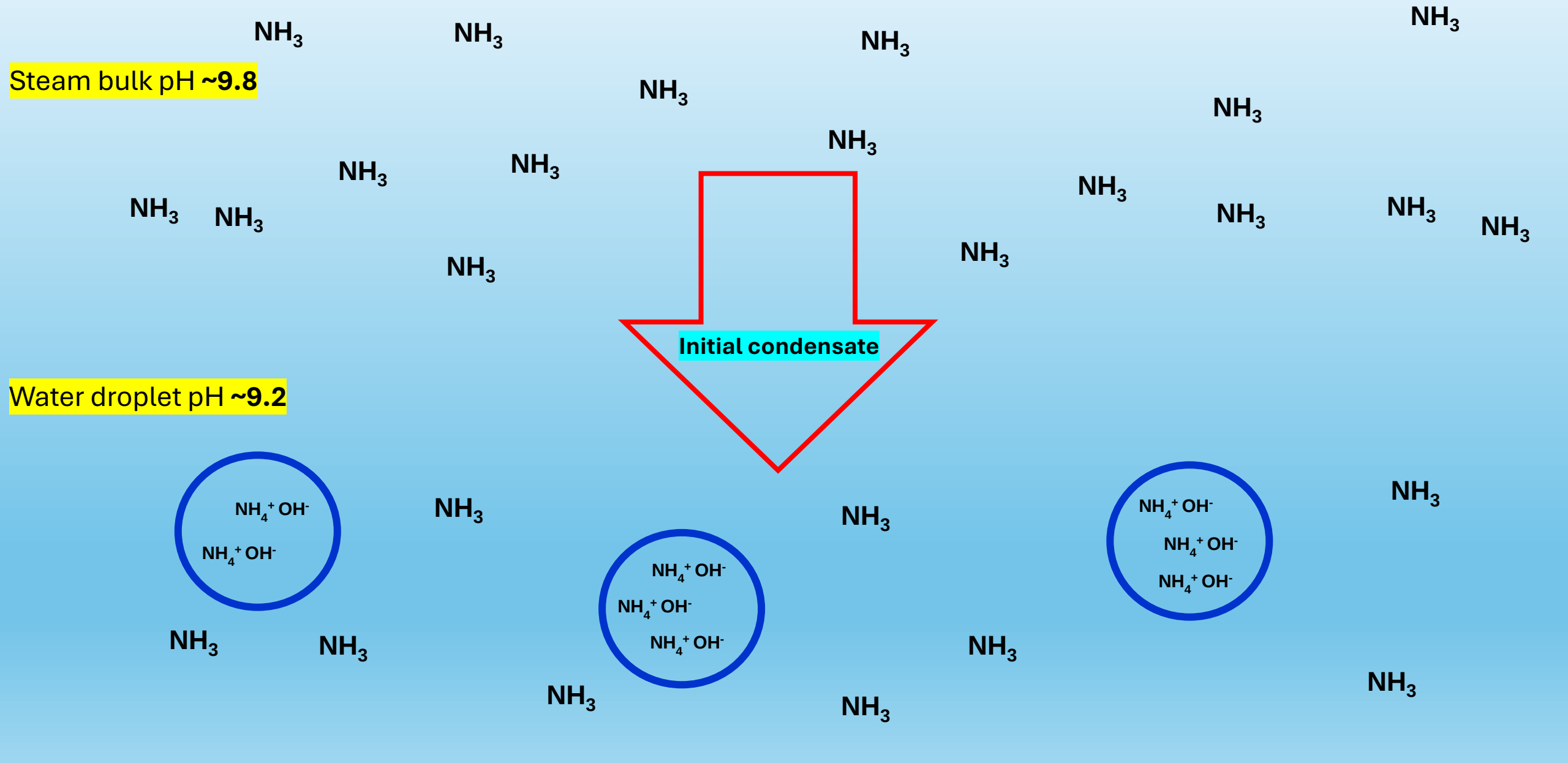
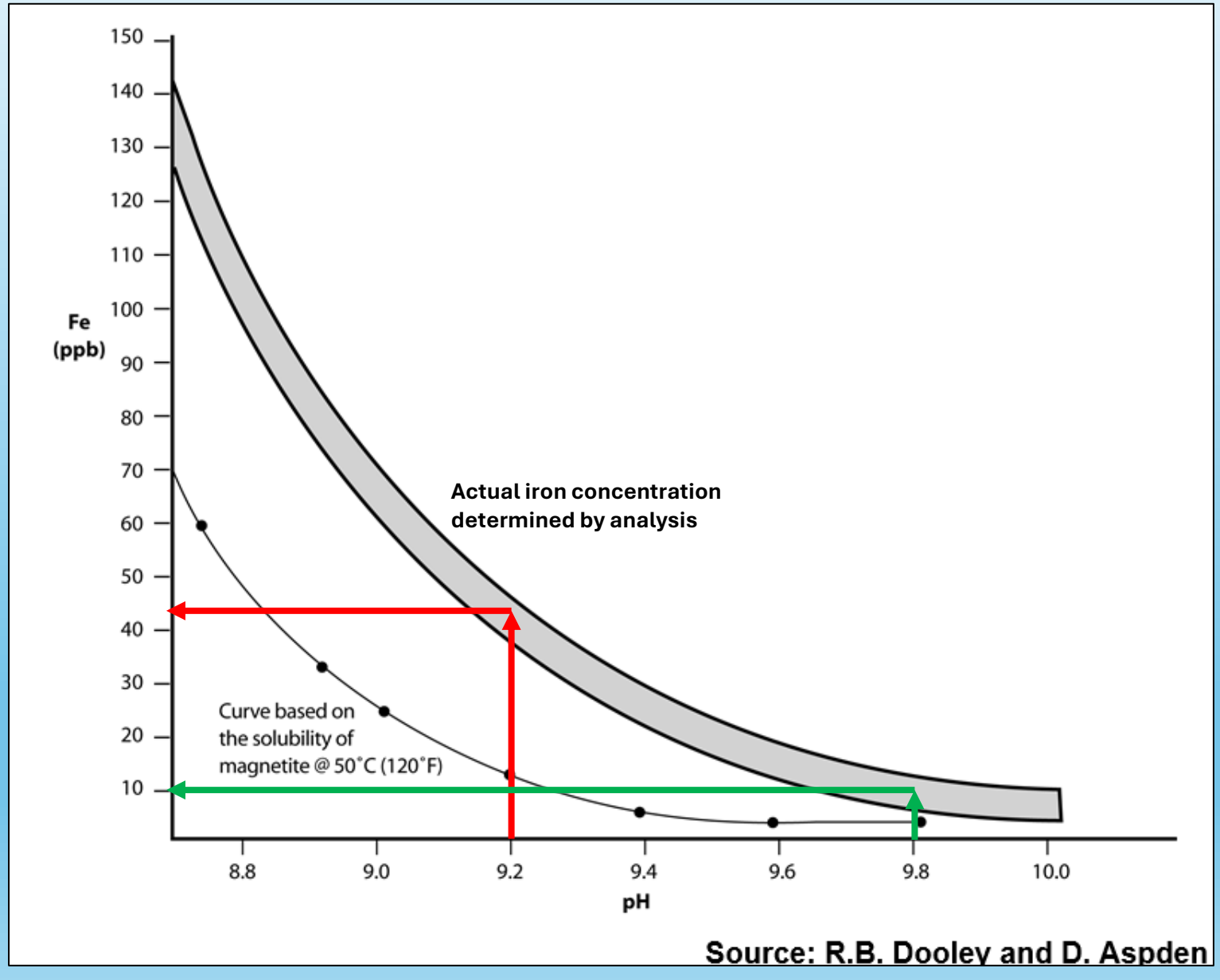
Condensing Steam with NH_3 Treatment



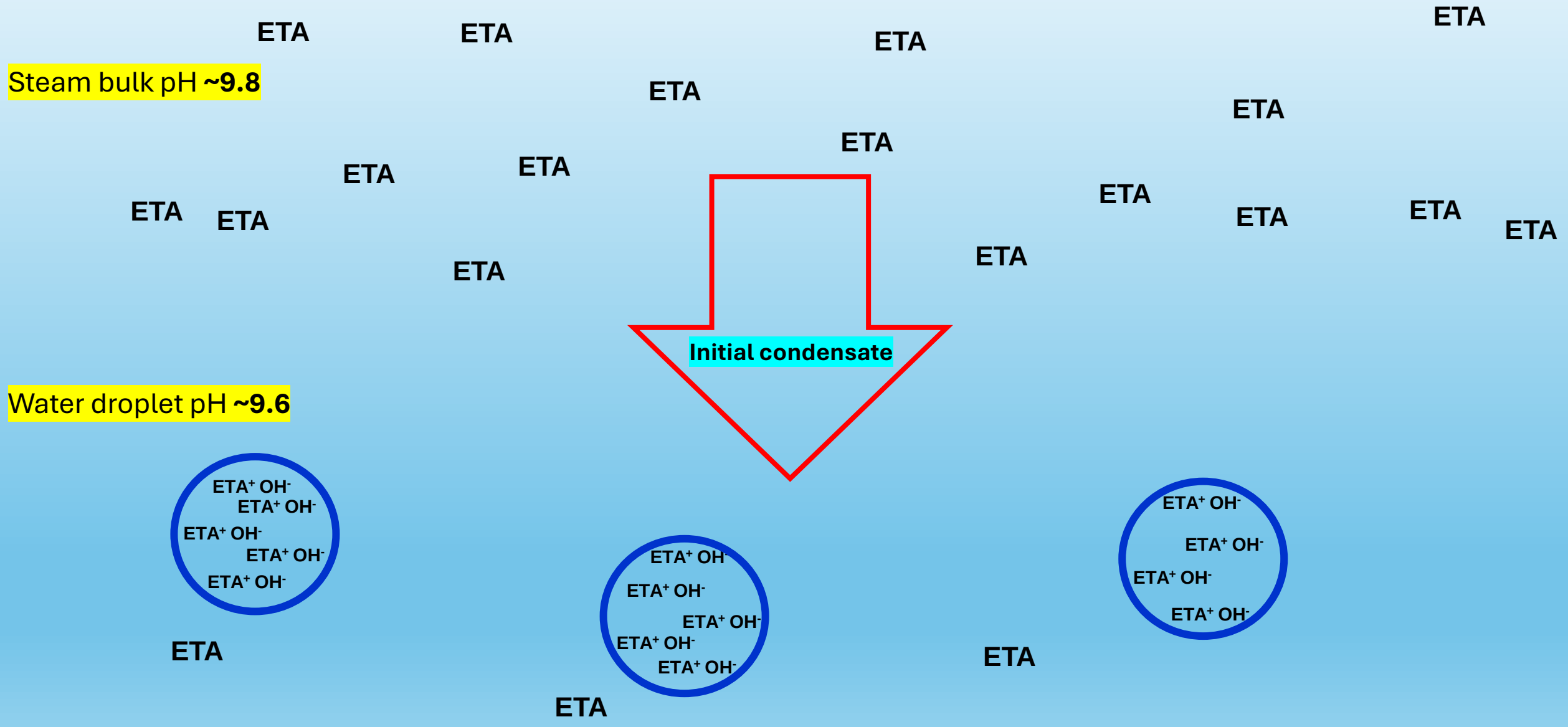
Iron Solubility Graph: [Fe] vs pH

ammonia



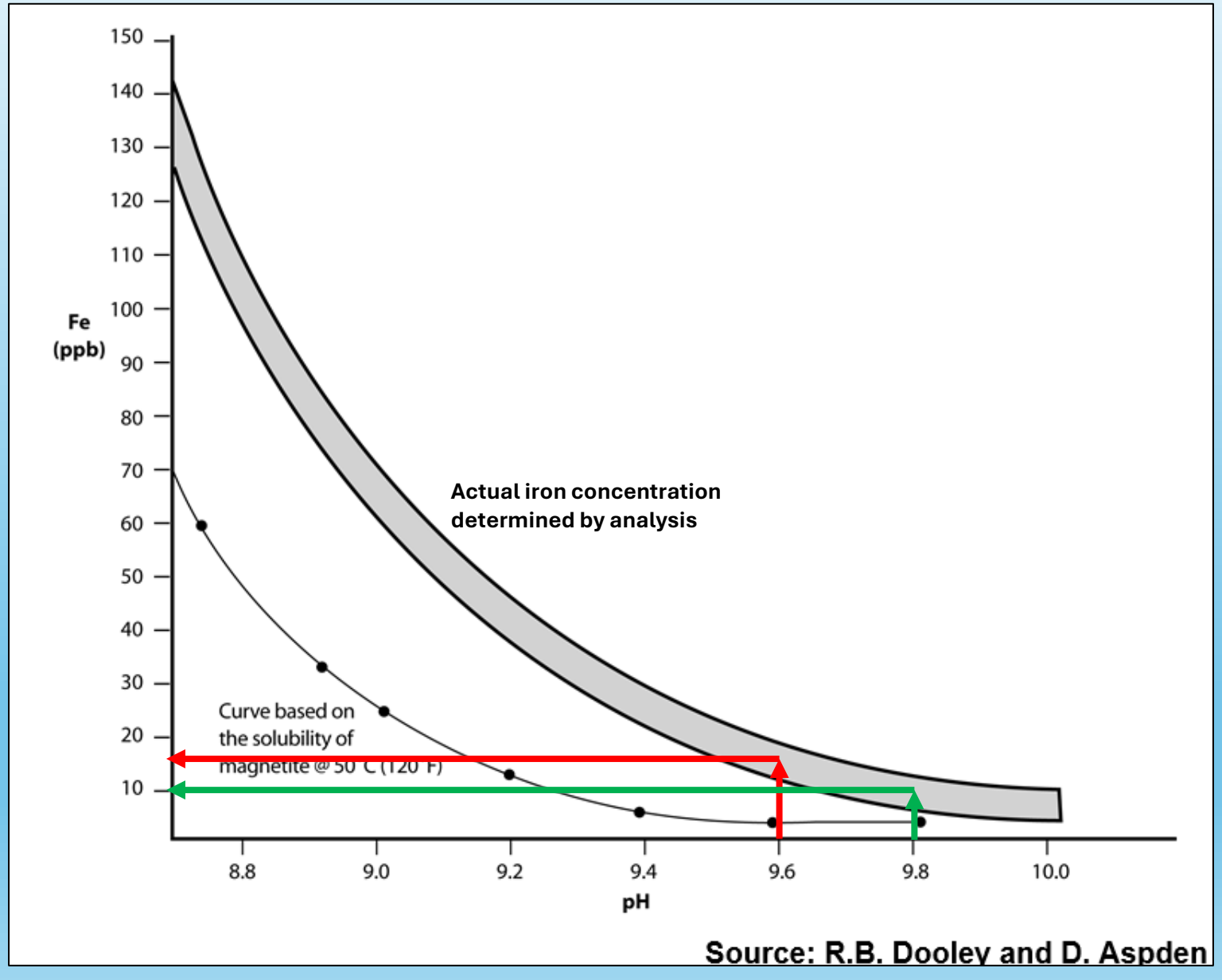
Condensing Steam with a Neutralizing Amine Treatment, Ethanolamine (ETA)

more ETA proportions into initial condensate droplets than does NH_3



Iron Solubility Graph: [Fe] vs pH

ethanolamine



Complication with neutralizing amines: decomposition in steam cycle

Ethanolamine decomposition in high-temperature steam:

$$CH_3\text{-}CH_2\text{-}NH_3 + H_2O + \text{Heat} \longrightarrow \text{formic acid / acetic acid}$$

These acids mitigate, to some extent, the benefit of amine pH control in early condensate. Specific decomposition extent is unit-specific such that formic acid / acetic acid, or rather their anions formate and acetate, must be measured in order to calculate the extent of the effect of these acids on early condensate pH.

As a result, optimizing amine feed can be difficult.

Requirement for evaluating the effect of any steam cycle chemistry changes:

1. Iron transport monitoring.

2. Periodic examination of steamside ACC surfaces.

Condensate Polishing in ACC plants

Condensate polishing can remove corrodents from various sources, but the most common contaminant in ACCs that can be removed by condensate polishing is carbon dioxide, which is relatively benign. The need for condensate polishing in combined cycle plants should be carefully evaluated.

Condensate Polishing with Ammonia treatment

- ACCs typically operate near pH 10 with ammonium hydroxide
- At pH 10, both cation and anion resin are ineffective at capturing and retaining monovalent cations and anions:
  - NH_4^+ is at high concentrations at pH 10 and displaces e.g. sodium Na^+
  - OH^- is at high concentrations at pH 10 and displaces e.g. chloride Cl^-
- Divalent cations and anions are better retained -- Ca^{2+}, SO_4^{2-}

➢ Powdered resin polishers are rendered meaningless at pH 10

➢ Deep bed polishers are poorly-effective at pH 10

Condensate Polishing with Ethanolamine treatment

- Steam cycles with ETA may be controlled at a lower system pH than those using ammonia, because the early condensate pH is the primary consideration for ACC plants.
- The extent of polisher capture of ETA and its decomposition products needs to be better defined, but will be important for ACC units with condensate polishing.
- Some research has shown that neutralizing amines such as ETA are difficult to remove from anion resin after being captured, but this has not been studied in detail.

Condensate Filtration for ACCs

- Particulate iron removal from ACC condensate is a priority need for all ACC plants
- Powdered resin polishers are very effective for particulate removal, but removal of ionic constituents (IX resin) is not particularly helpful
- Deep bed polisher equipment may remove particulates but the polisher / resin is not particularly helpful
- Full-flow condensate filtration very effectively removes particulate iron from condensate

Summary

The application of neutralizing amines has the potential to significantly lower corrosion risk for carbon steel in air-cooled condensers. The optimal application of neutralizing amines is not straightforward and requires careful planning and monitoring of the amine and its decomposition products. Routine and consistent monitoring of iron transport and inspection of steamside surfaces of the ACC are essential to understand and optimize chemistry changes.

FACC: Flow-Accelerated Condensate Corrosion (form of 2-phase FAC)

Carbon Steel, Condenser Steam-side

Typical macroscopic appearance:

- black (magnetite) patches, sometimes red (hematite)
- shiny reflective metal *or* flash rust
- erratic patterns, impression of flow-influenced

Condenser 1

Condenser 2

Condenser 3

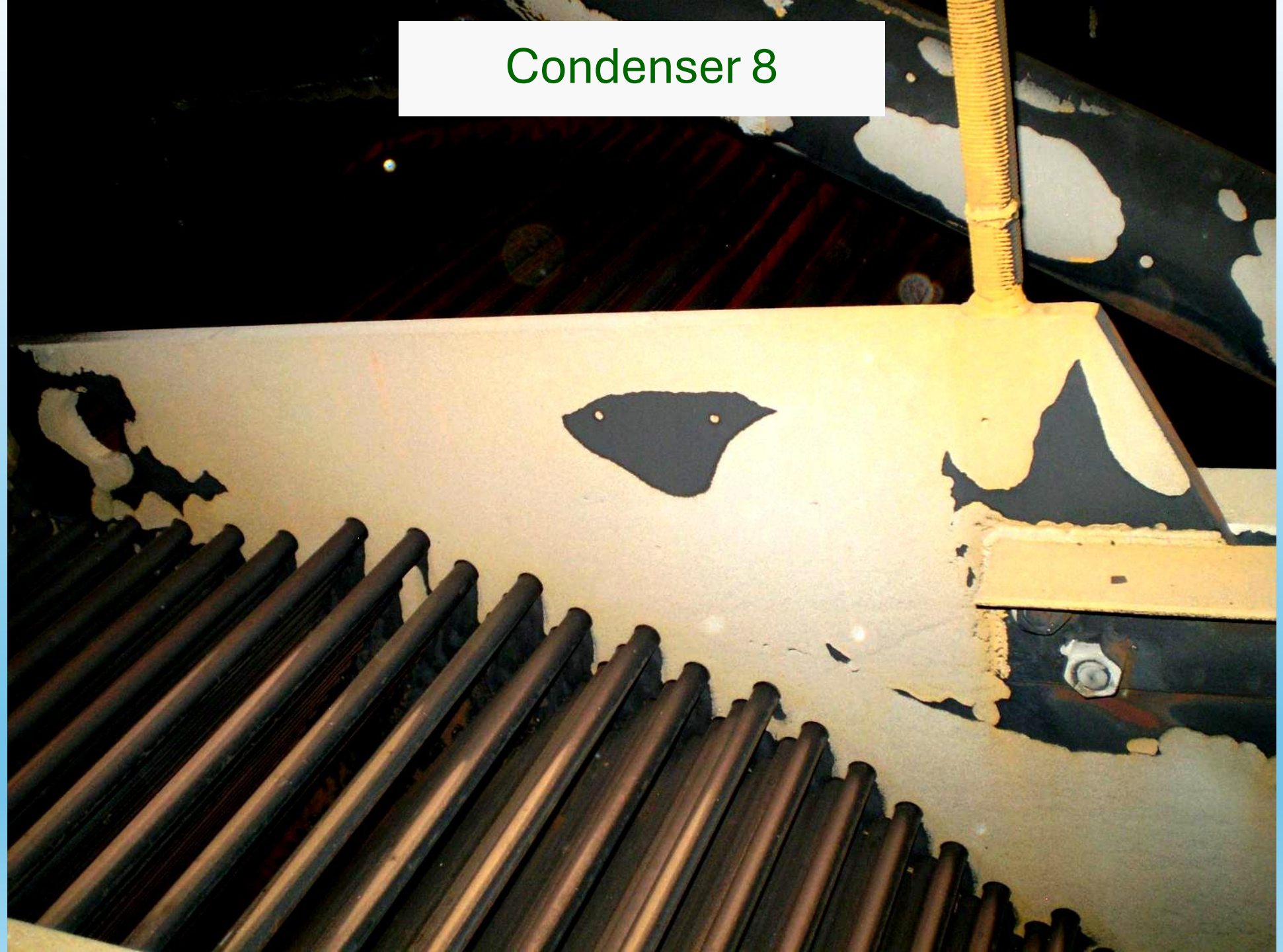
Condenser 4

Condenser 5

Condenser 6

Condenser 7

Condenser 8



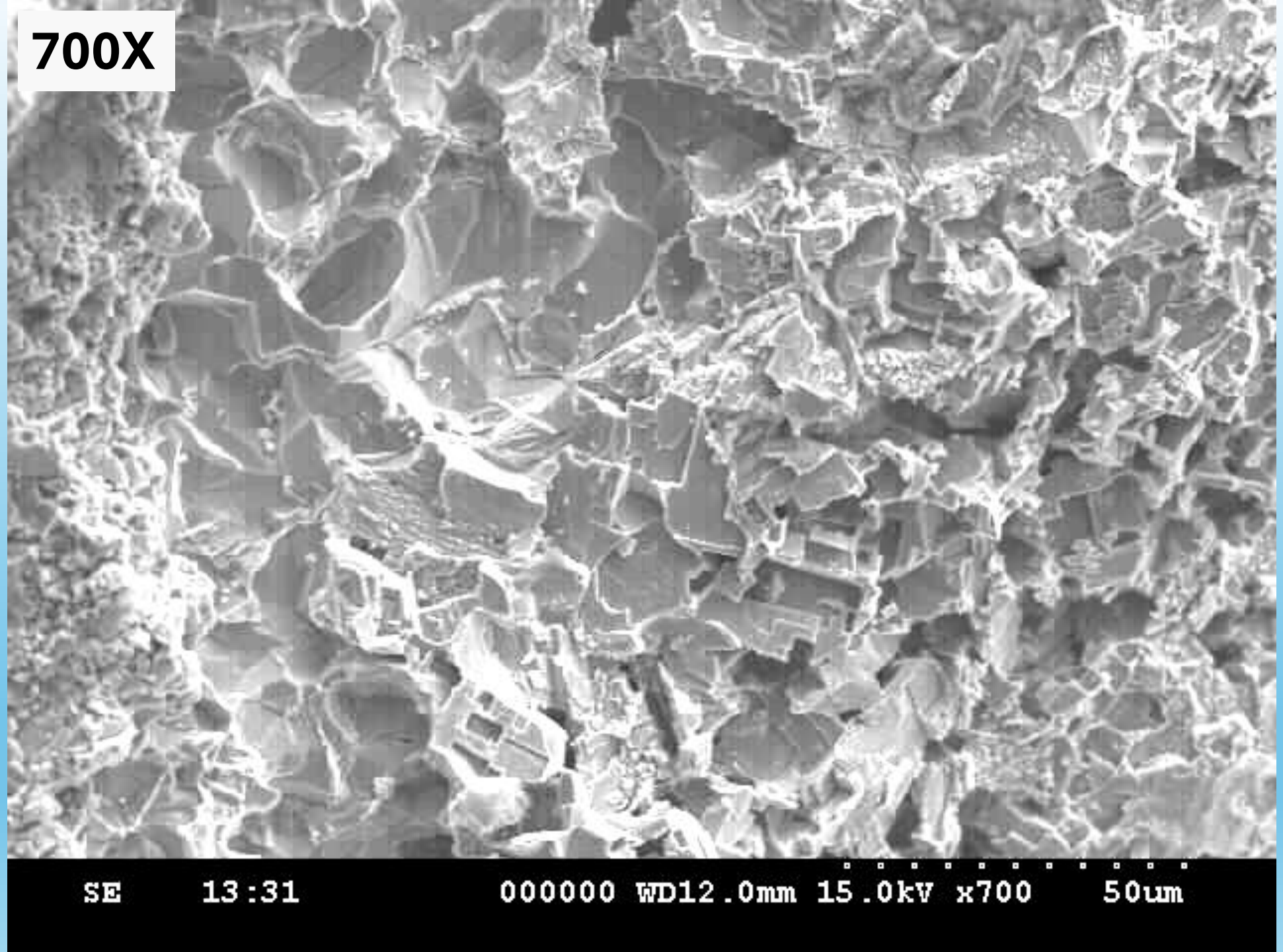
Condenser 9

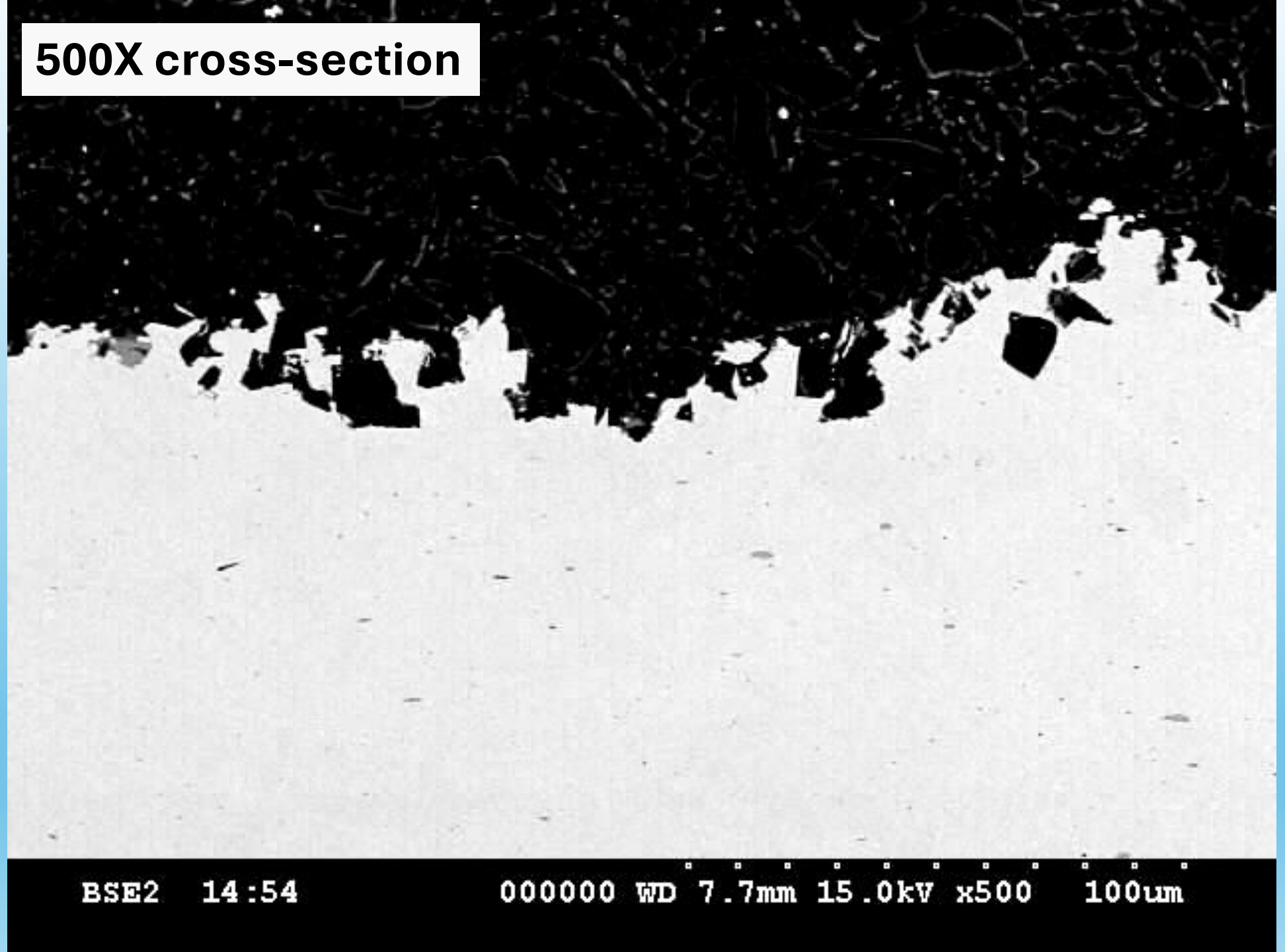
Condenser 10

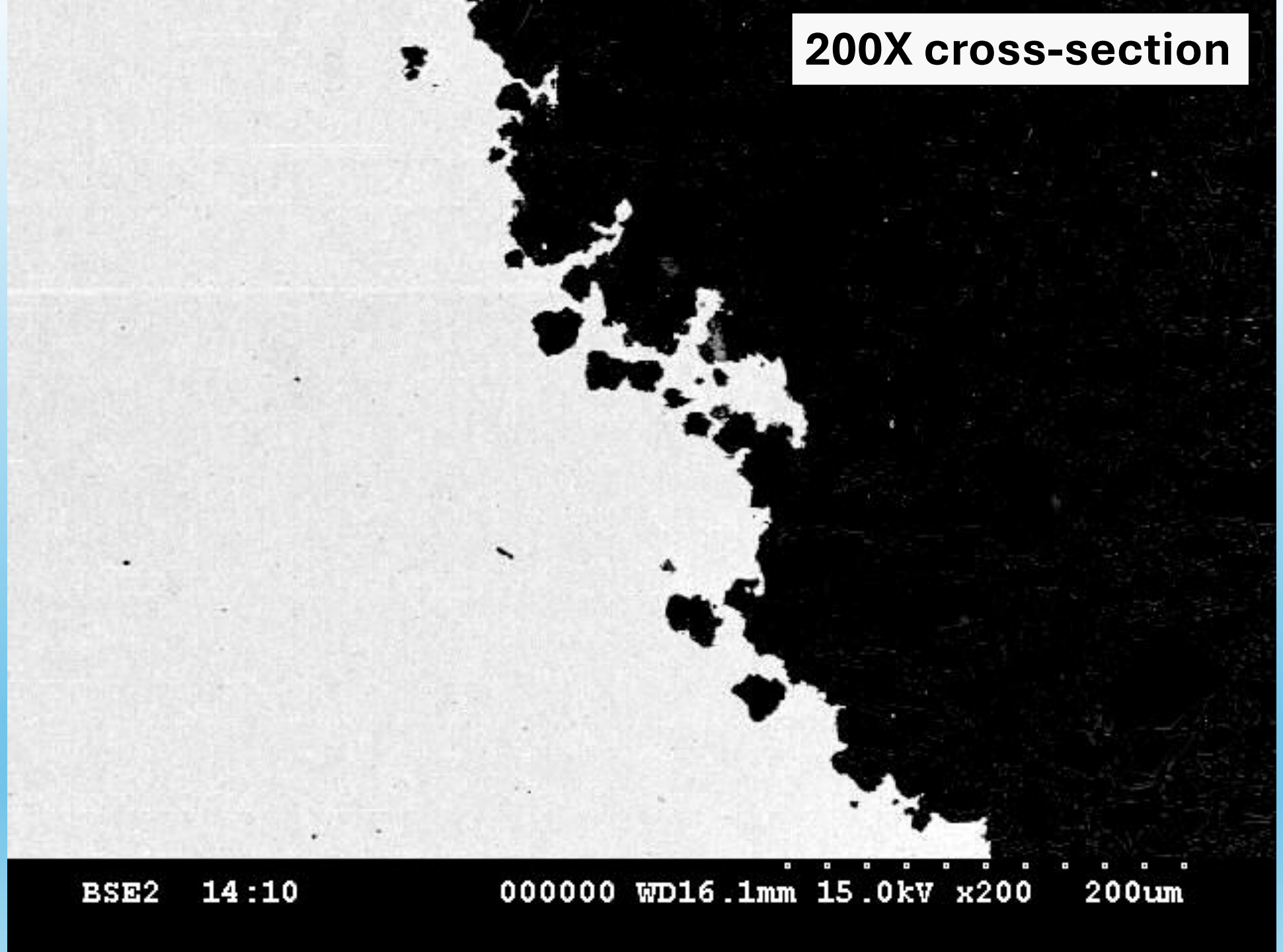
Condenser 11

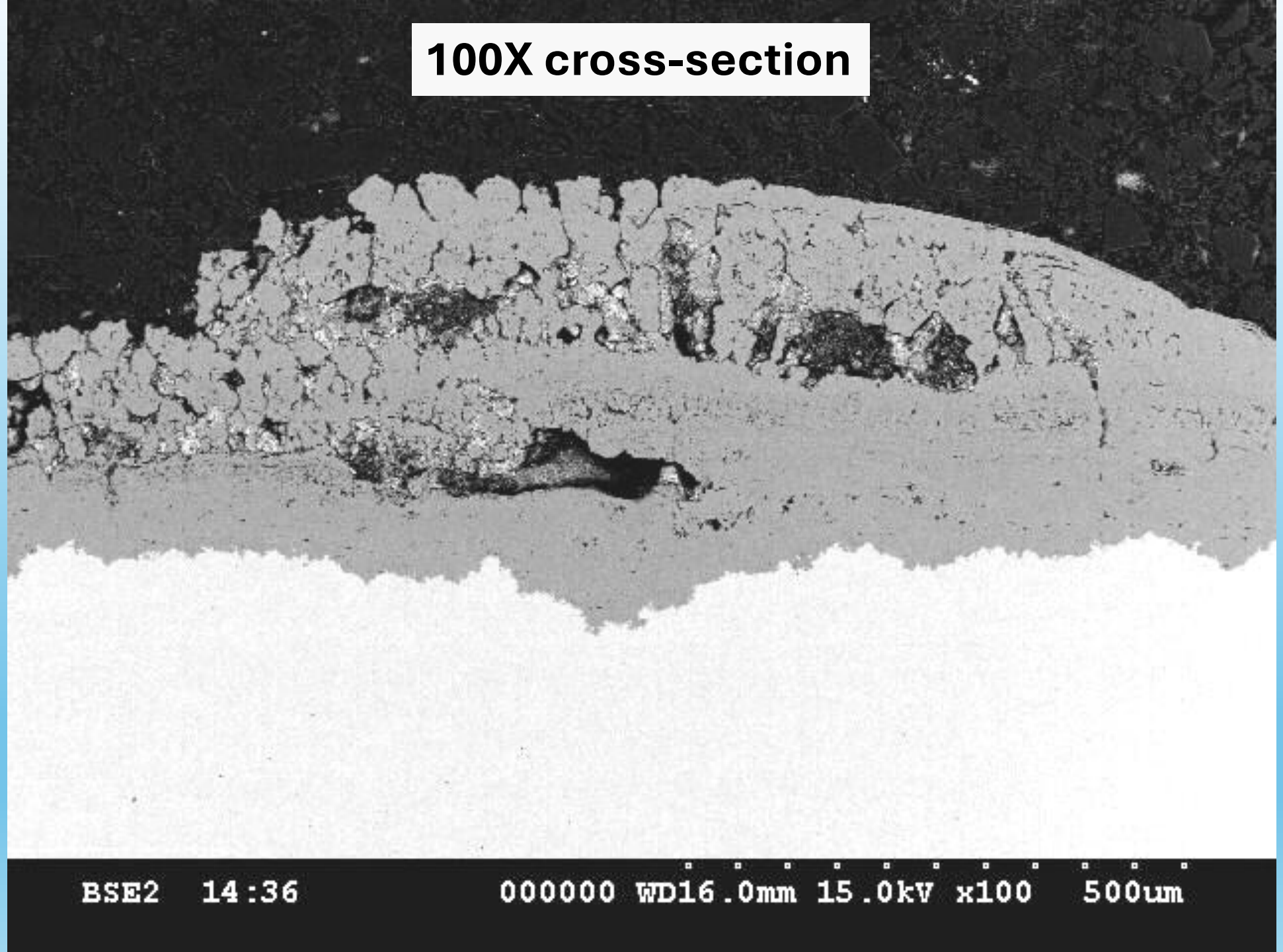
Microscopic Observations:

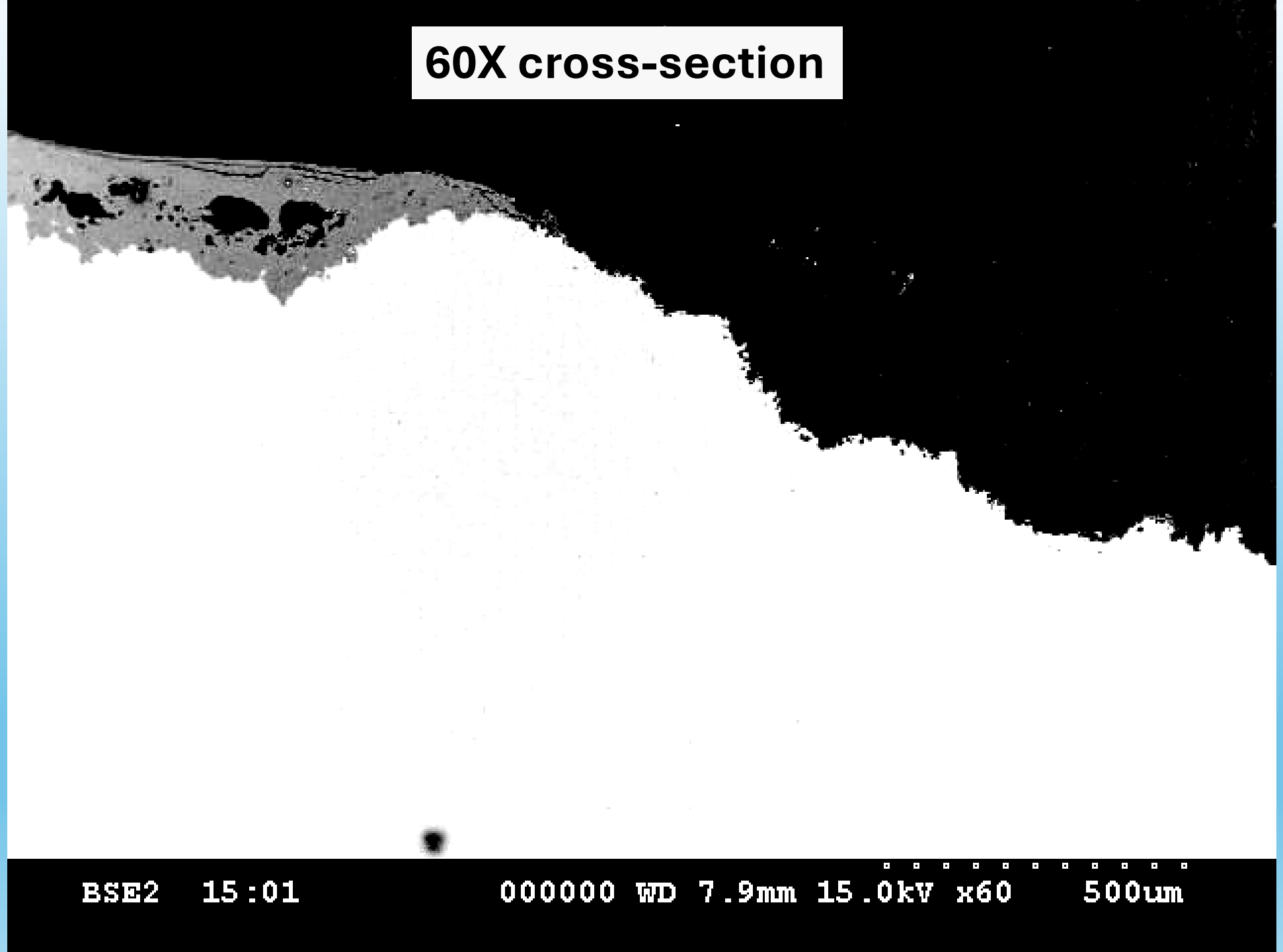
- exposed metal surfaces are faceted (intergranular, IG)
- exposed metal in cross-section is faceted (IG)
- metal surface structures are not smooth
- iron oxide is commonly thick and adherent
- exposed metal adjacent to oxide is thinned


700X
SE 13:31 000000 WD12.0mm 15.0kV x700 50um


500X cross-section
BSE2 14:54
000000 WD 7.7mm 15.0kV x500 100um


200X cross-section
BSE2 14:10
000000 WD16.1mm 15.0kV x200 200um


100X cross-section
BSE2 14:36
000000 WD16.0mm 15.0kV x100 500um


60X cross-section
BSE2 15:01 000000 WD 7.9mm 15.0kV x60 500um


14 months

Proposed Corrosion Mechanism

1. magnetite forms on carbon steel

$$3Fe^{o} + 4H_2O \rightarrow Fe_3O_4 + 4H_2$$

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   - separation promoted by H_2 gas and flow

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4. Relative stability is reached in the corrosion process
   - *"bare metal" serves as cathodic site to slow oxidation of metal under oxide*

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2. oxidation of steel progresses beneath oxide: general / intergranular
3. Release of metal / oxide resulting from intergranular corrosion
4. Relative stability is reached in the corrosion process
5. Changes in pH will disrupt stability
   - *lower pH will accelerate further FACC*
   - *higher pH will maintain or reverse FACC*

FACC Reduction / Mitigation

- material resistant to intergranular corrosion
- reduced velocity
- chemistry – higher pH in early condensate
- particulate filtration

Conclusions

Corrosion of carbon steel in WCCs and ACCs appears to be different from traditional FAC mechanisms, and may require different mitigation approaches.

The exact mechanism of FAC is not completely understood.

Discussion / Questions