**Manuscript Outline**

1. **Introduction**

* The necessity of using waste brine to valorize for chemical production. The background of BMED and its application
* The scaling problem in BMED treating brine. Review previous studies on scaling in BMED
* Define the research gap 🡪 There is no comprehensive research of scaling in BMED. Relevant studies results. Introduce the scaling mechanism in ED
* Objective 🡪 the focus of our study and its significance.

1. **Material and Methods**
   1. **Lab-scale BMED stack**

* Chambers, chamber thickness, membranes.
* Figure 1. Lab-scale BMED stack
  1. **Protocol**
* Mode, composition of SWB (baseline: NaCl)
* Test process description: volume of solutions, flow rate, current density.

Section S1: The composition of model seawater brine

Table S1. The composition of model SWB

* 1. **Scaling characterization and BMED performance analysis**
     1. **Scaling characterization**
* SEM, EDS
* Turbidimeter
* XRD
  + 1. **BMED performance analysis**
* Conductivity, pH
* ICP-OES
* System resistance (total, chamber, membrane)

Section S2: System electrical resistance calculation

Figure S1. the stack to test electrode resistance.

Figure S2. The voltage change with current.

1. **Results and Discussion**
   1. **Characterization of scaling on different IEMs in BMED stack**

* When BMED treat NaCl, there is no scaling.

Section S3. Characterization of pristine membranes

Figure S3 Photo of pristine membrane + FESEM + EDS

* However, when it treats SWB, there is severe scaling on membranes and in chambers

Figure 2. Photo of membranes in NaCl + FESEM + EDS; Photo of scaled membranes in SWB + FESEM + EDS

SI section S4: Scaling formation in chambers

Figure S4. Photos of solution at the beginning of testing and at the end of testing (NaCl & SWB).

Table S2. Turbidity of solutions at the beginning and end of testing.

* Explore the scaling composition

Section S5. The composition of scaling (preparation of scaling crystals)

Figure S5. XRD result

* 1. **Influence of scaling on BMED performance**
* BMED performance difference

Figure 3. (a) voltage change with time; (b) acid and base production; (c) pH change in salt chamber; (d) resistance change with time (total, membrane, chamber).

SI section S6: BMED acid/base production rate, SEC and system electrical resistance

Figure S6. The conductivity change of salt, acid and base.

Figure S7. Acid/base production rate with time. 🡪 Figure 2b

Figure S8. SEC

* 1. **The scaling mechanisms in BMED**
     1. **Scaling formation in the bulk solution and on membranes.**
* The scaling formation mechanism. Solubility product exceeds limitation near membrane surface. scaling will form on membrane. If it exceeds limitation far away from membrane, it will form in bulk solution. The quantification shows the total scaling in the system.

Figure 4. Quantification of scaling. (a) mass of Ca/Mg scaling with time; (b) reduction percentage of Ca/Mg with time.

Section S7: The method to quantify scaling 🡪 equations.

Figure S9. The concentration change in acid chamber.

* + 1. **Scaling formation on CEM**
* Scaling on membrane facing SWBC: (1) water splitting (pH increase in salt chamber); (2) OH- leakage (transport number).
* Scaling on membrane facing BC: (1) concentration change in base chamber.
* Summary: the formation of scaling on both side of CEM (schematic diagram)

Figure 5. (a) Concentration of Ca/Mg in salt chamber; (b) Concentration of Ca/Mg in base chamber.

Figure 6. (a) Schematic diagram of scaling formation mechanisms on both sides of CEM. (b) Transport number of counterions with different membranes.

Section S8: The calculation of transport number

Figure S10. The stack diagram

Section S9: The cross-section of pristine and scaled CEM and BPM

Figure S11. Cross-section

* + 1. **Scaling formation on BPM**
* The high concentration of OH- on BPM surface

Figure 7. (a) schematic diagram of scaling formation on BPM. (b) The concentration of acid/base with unscaled BPM and scaled BPM.

* 1. **Reversibility of membranes in BMED**

Figure 8. Performance change before scaling, after scaling and after cleaning.

1. **Implications**

* The findings in the study 🡪 scaling formation, its influence on performance and mechanisms
* Implication