Effect of Impurities in Brine on Membrane Performance and its Performance Recovery

May 2008
AGC Chemicals
ASAHI GLASS Co., LTD.

AGC Chemicals
Chemistry for a Blue Planet

AGC

Today Presentation consists of

1. Model of Membrane Damage by Impurities
2. Introduction of C.E. Recovery Methods
3. Verification of Effects by these Methods with Labo. Cell & Commercial Plants
4. Durability of F8020 against Impurities
5. Introduction of F8020SP

Main Effect of impurities in Brine

	Decline of C.E.	Increment of CV	Quality of NaOH
Cation	Ca Sr Ba Al Hg	Mg Ni Fe Al	
Anion	I SO_4		ClO_3
Others	SiO_2 Organic	SiO_2 Organic	

AGC Chemicals
Chemistry for a Blue Planet

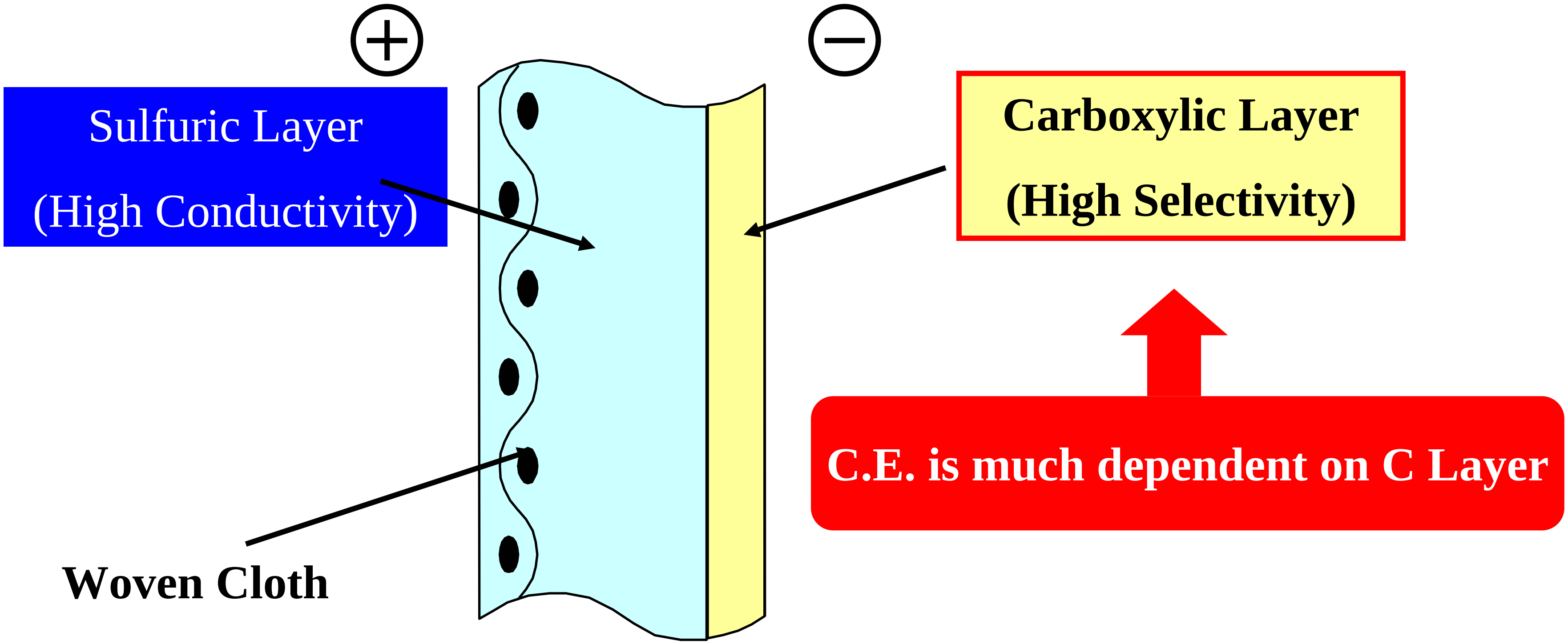
AGC

Main Effect of impurities in Brine

	Decline of C.E.	Increment of CV	Quality of NaOH
Cation	Ca Sr Ba Al Hg	Mg Ni Fe Al	
Anion	I SO_4		ClO_3
Others	SiO_2 Organic	SiO_2 Organic	

Today Presentation will be focused on C.E.

Basic Structure of Flemion



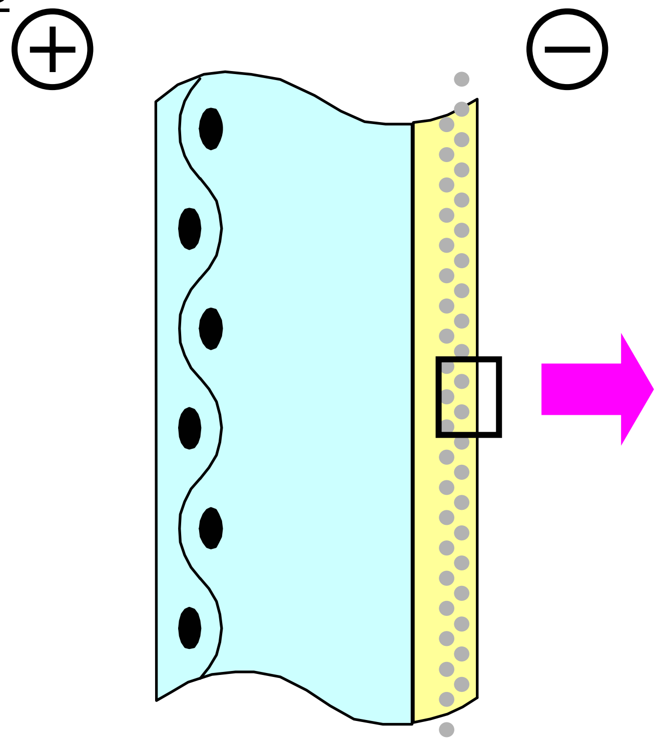
<u>Basically Membrane is composed of 2 Layers</u>

Precipitation of Impurities inside Membrane

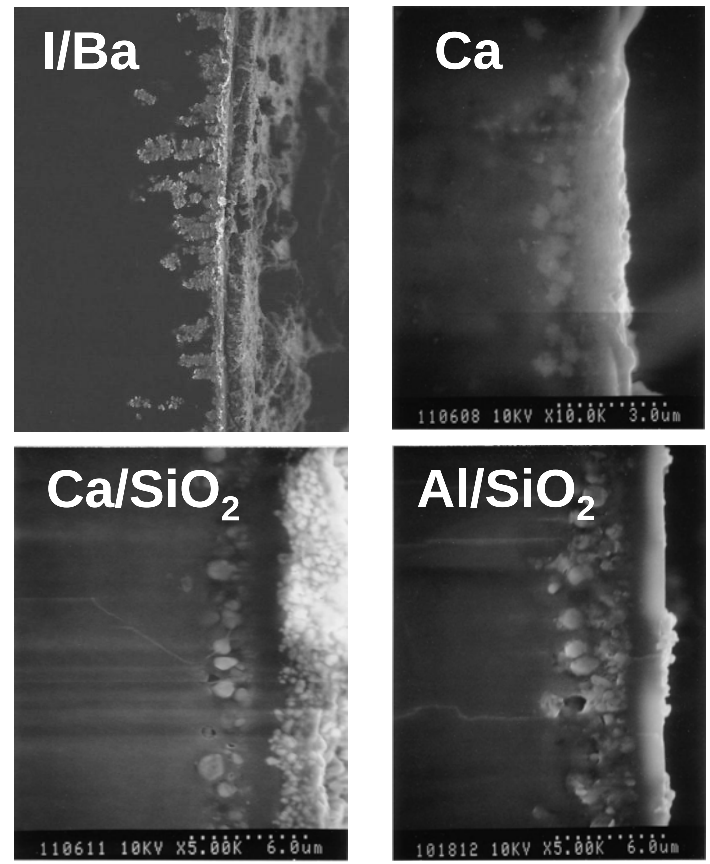
Impurities

Cation
- Ca
- Sr
- Ba
- Al
- etc.

Others
- I
- SiO_2
- etc.



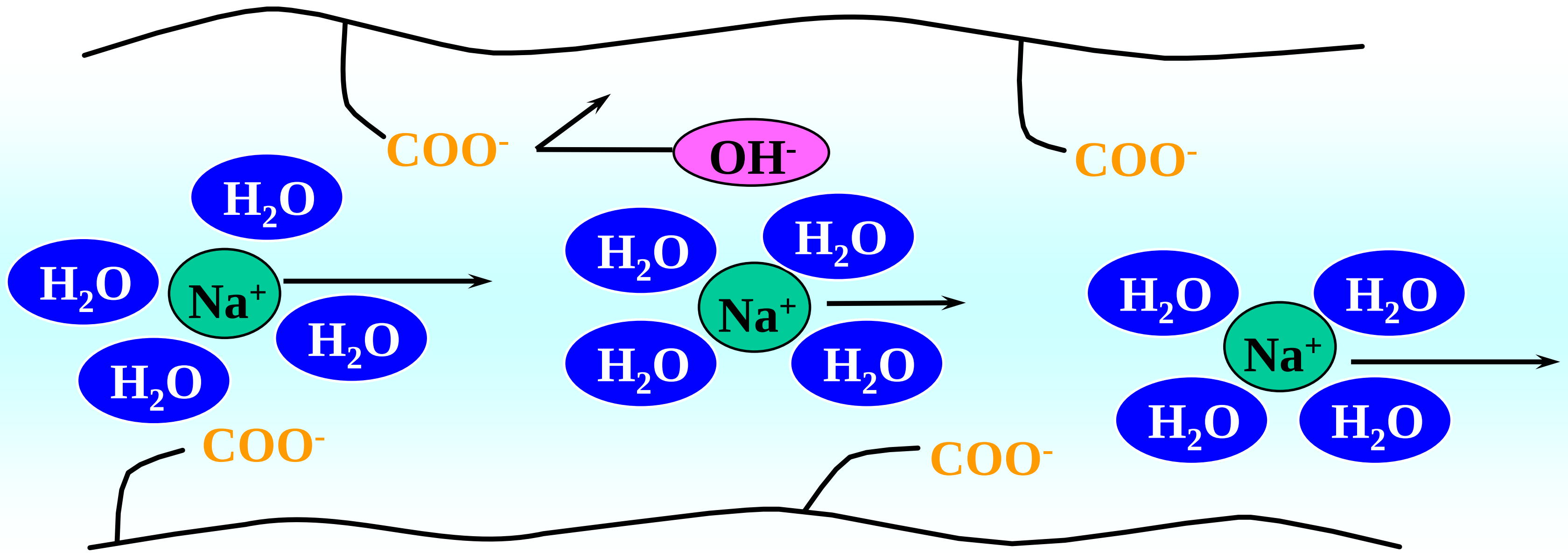
SEM of Impurities Precipitation



Impurity Precipitates in C-layer → CE decreases

Mechanism of High C.E. Performance

Normal State

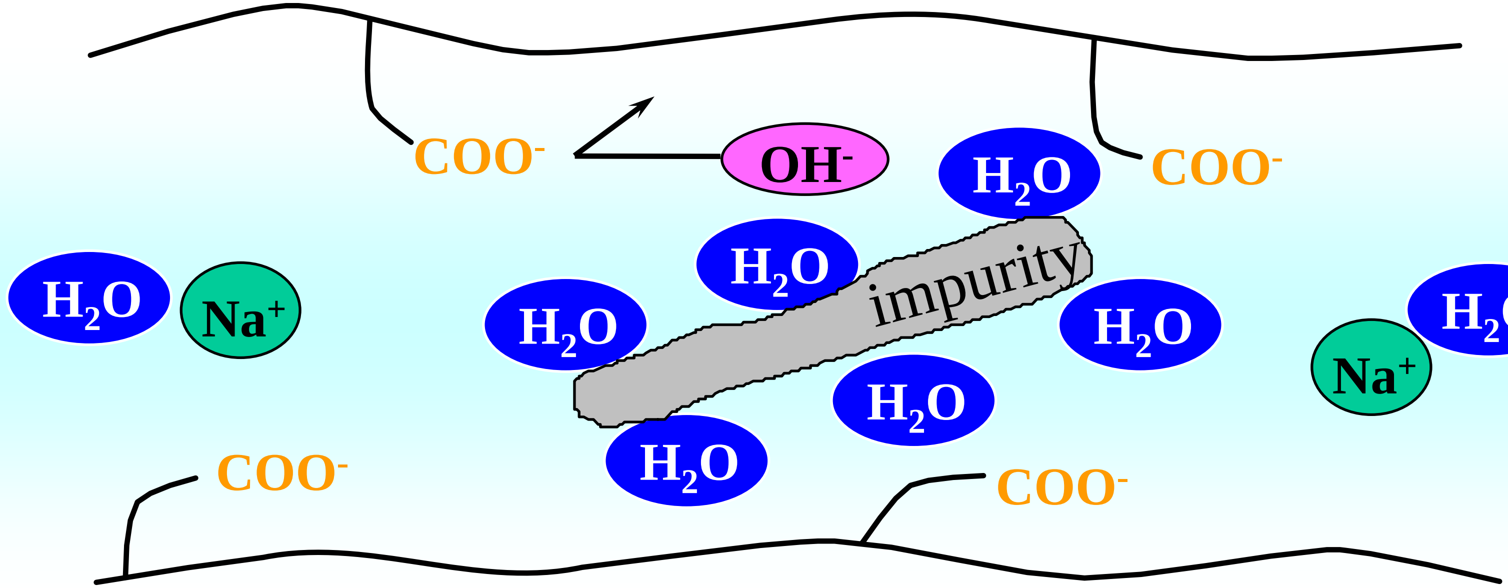


Anion(OH^-) can't pass through the membrane

due to the repulsive force of fixed negative charge

C.E. Decline due to Fine Particles Precipitation

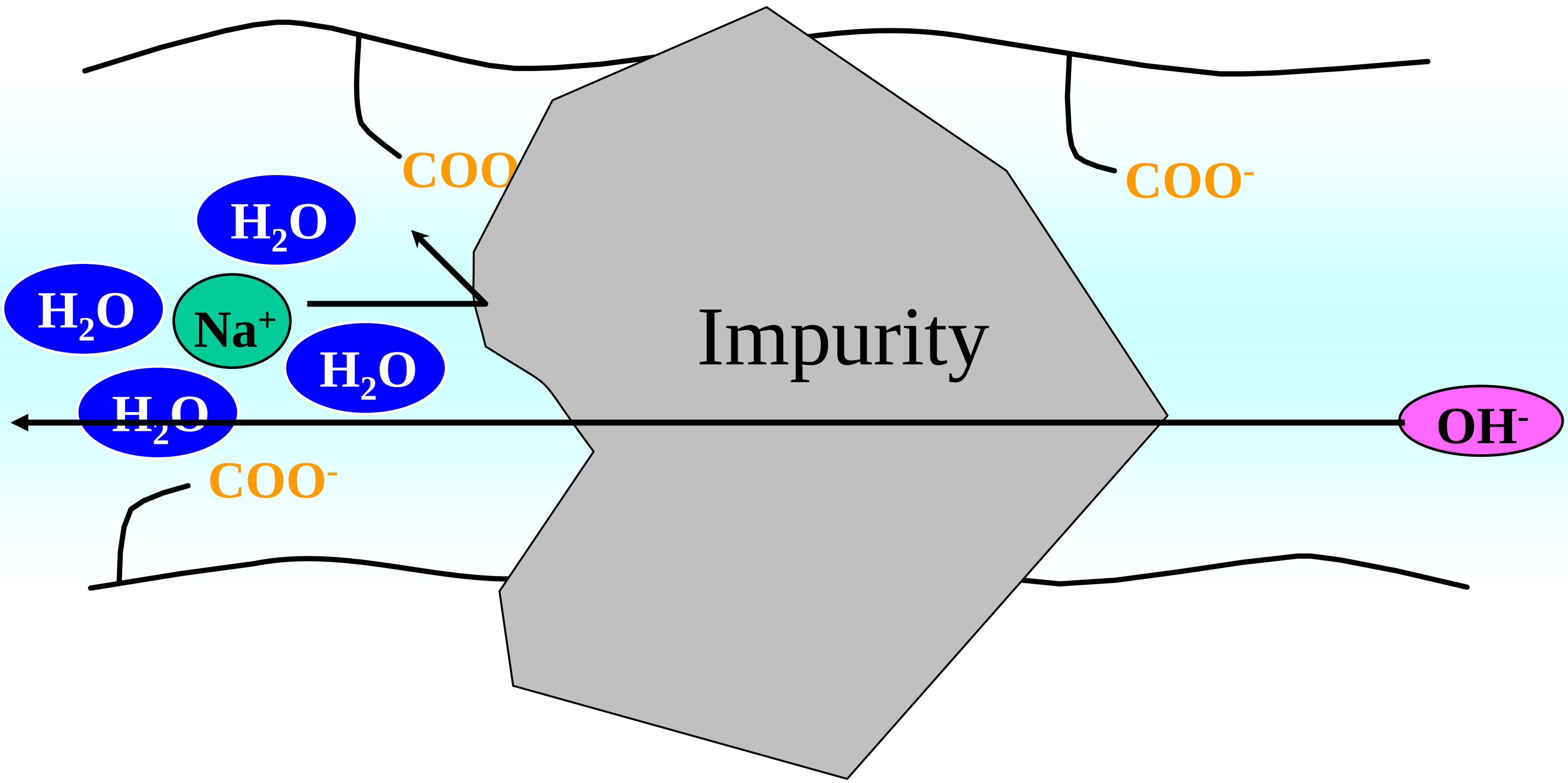
State of Fine Particles Precipitation



Dehydrated State ⇒ Decrease in Na Ion Mobility

C.E. Decline due to Large Particles Precipitation

State of Large Particles Precipitation



Ion Channel Destruction ⇒ OH- is easy to pass through the membrane

Q: Does C.E. recover after damaged by Impurity ?

1) What affects the recovery of C.E.?

→" Model of Impurities Precipitation"

2) What are the methods for recovery ?

→ Five kinds of methods

3) Are these methods actually effective ?

→ Simulation by Labo. Cell

- **Impurities additional Tests**
- **Tests with membrane used by Customers**

→ Examples of C.E. recovery in Commercial Plants

AGC Chemicals
Chemistry for a Blue Planet

AGC

Q: Does C.E. recover after damaged by Impurity ?

1) What affects the recovery of C.E.?

→" Model of Impurities Precipitation"

2) What are the methods for recovery ?

→ Five kinds of methods

3) Are these methods actually effective ?

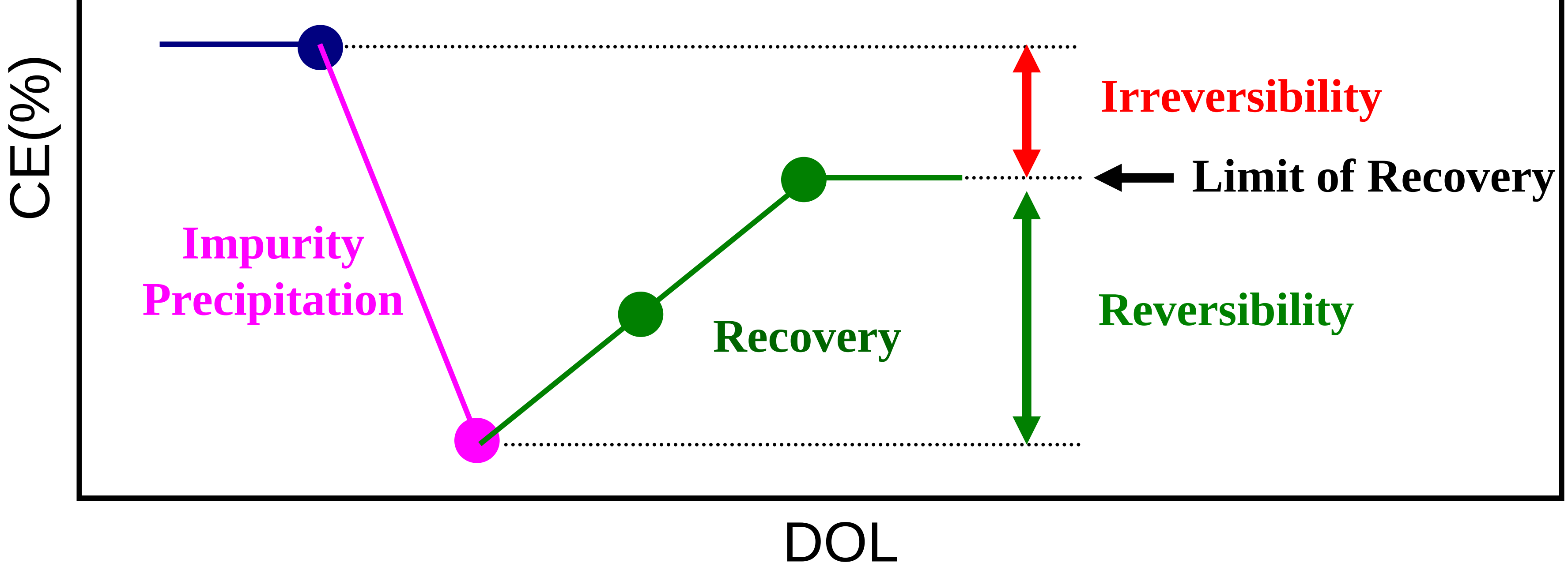
→ Simulation by Labo. Cell

- Impurities additional Tests
- Tests with membrane used by Customers

→ Examples of C.E. recovery in Commercial Plants

Model of Impurities Precipitation inside the membrane

In some cases, CE doesn't always recover completely after damaged by Impurities.

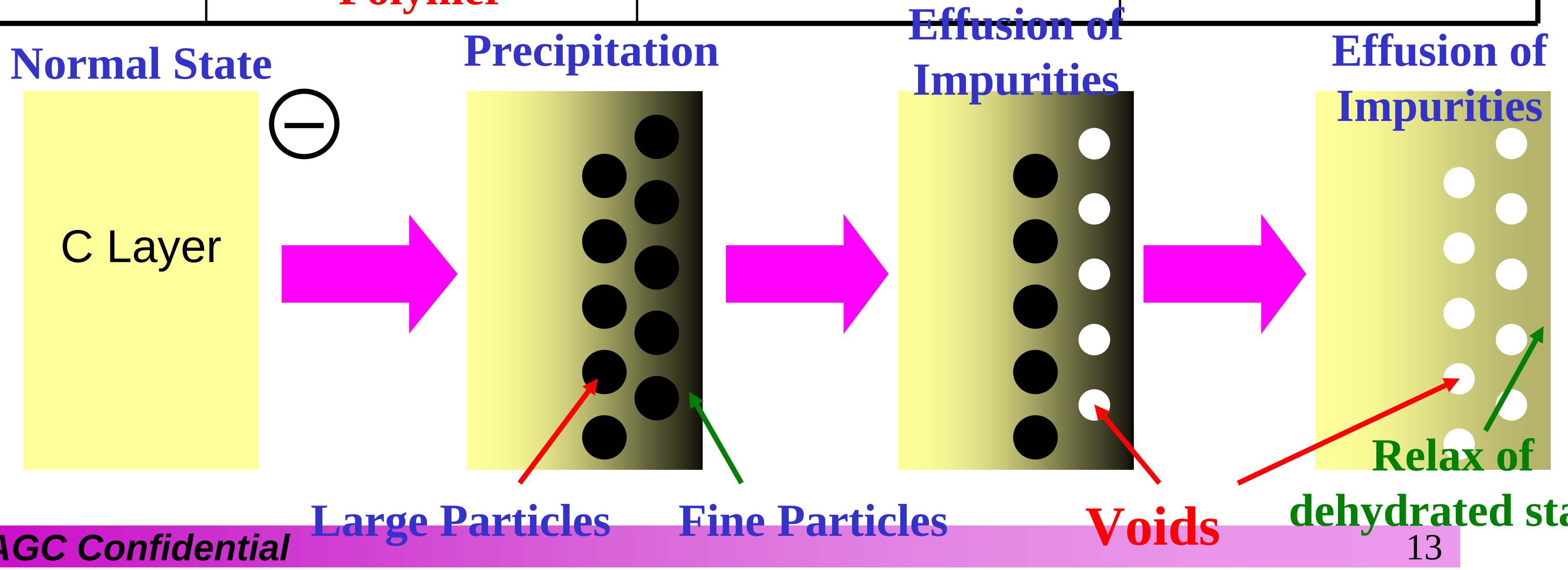


The Degree of C.E. Recovery is dependent on the kind of Damage by Impurity.

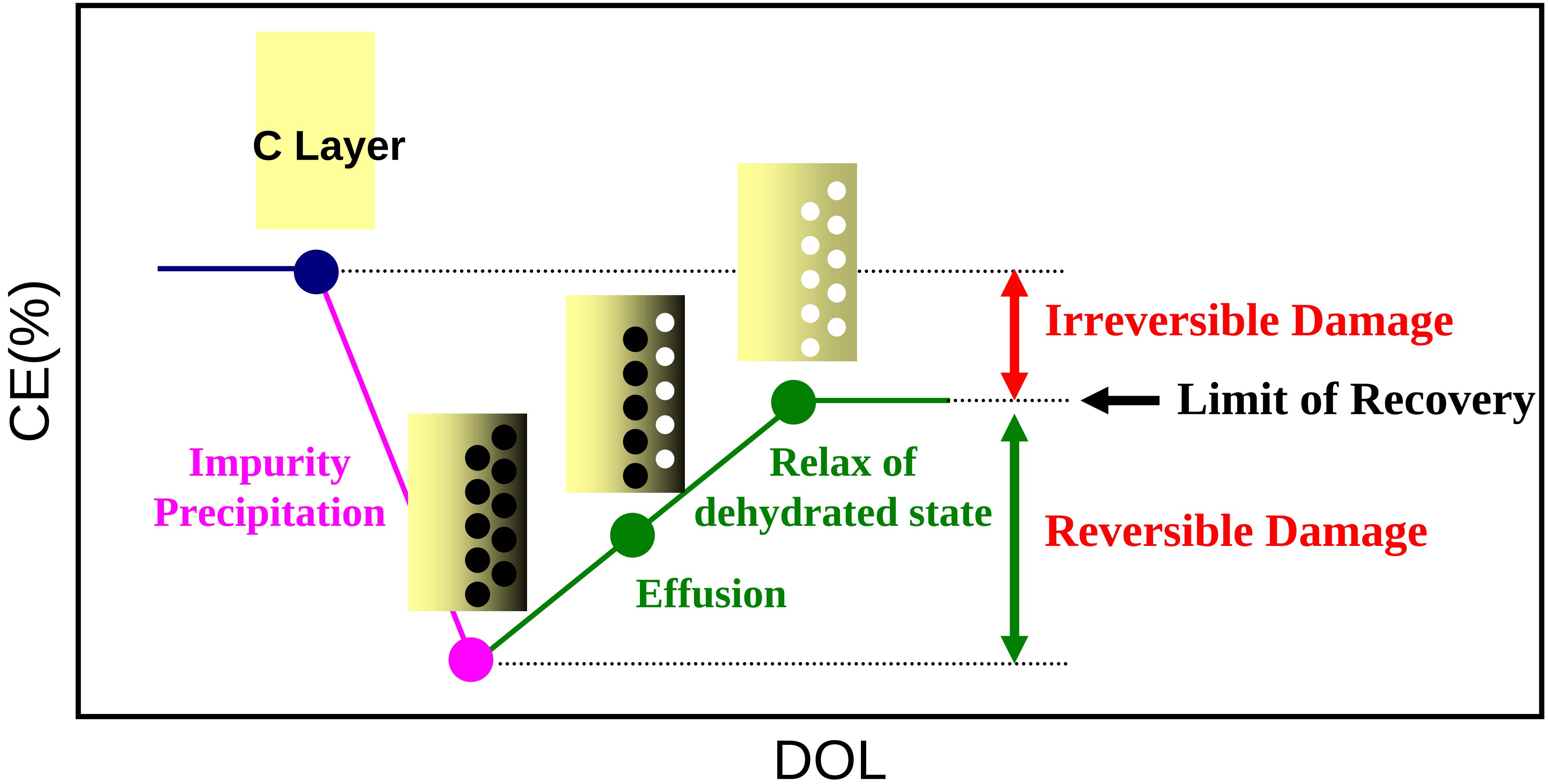
Model of Impurities Precipitation inside the membrane

<Hypothesis> **Damage depends on the size of Particles in the surface layer of C-layer**

Size	Effect of Precipitation	Effect of effusion	Damage
Fine	Dehydrated	Relax of dehydrated	Reversibility
Large	Destruction of Polymer	Remaining of Voids	Irreversibility

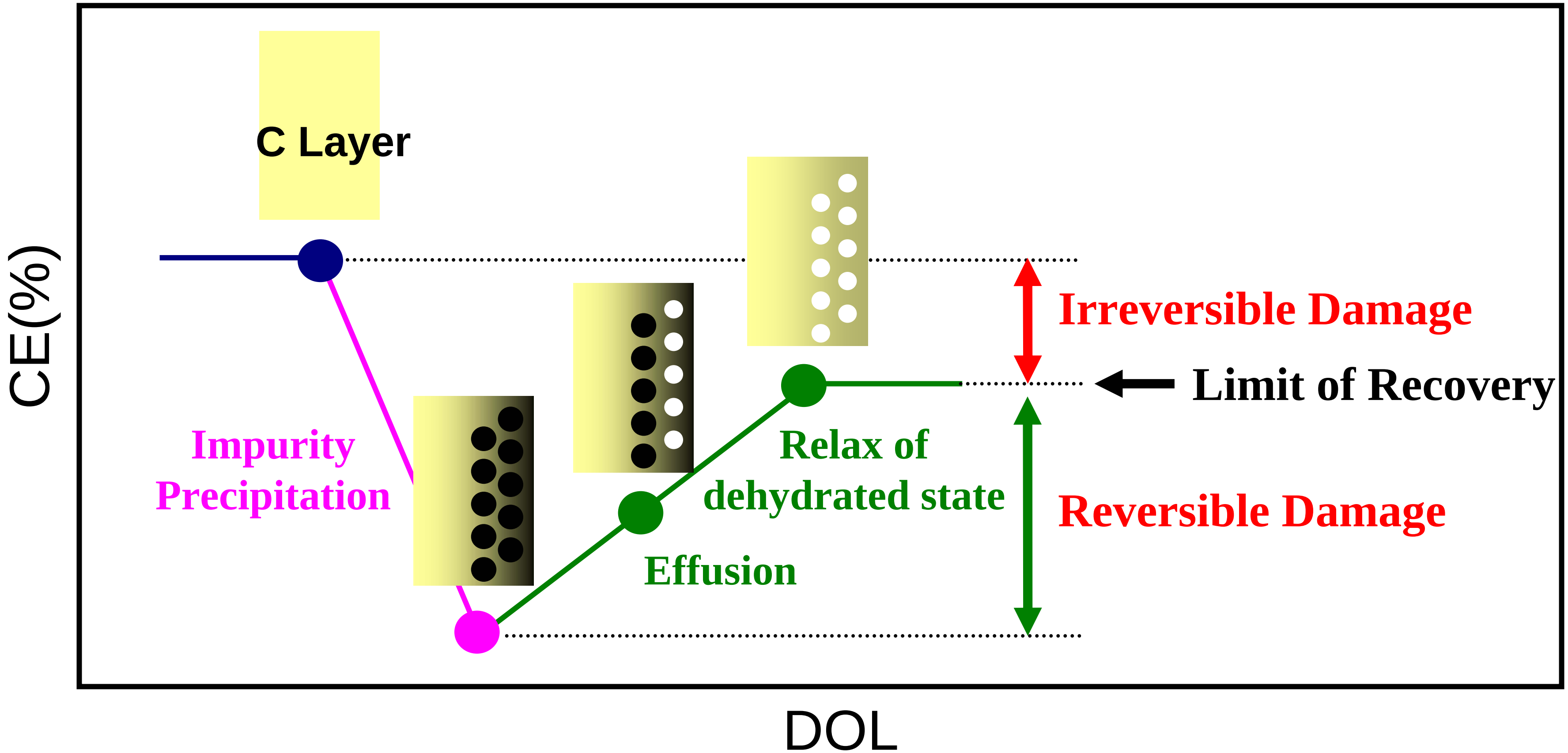


Model of Impurities Precipitation inside the membrane



<u>Reversible Damage can be recovered.</u>

Model of Impurities Precipitation inside the membrane



Key Points for Recovery are

1) Effusion 2) Relax from dehydrated state

Q: Does C.E. recover after damaged by Impurity ?

1) What affects the recovery of C.E.?

→" Model of Impurities Precipitation"

2) What are the methods for recovery ?

→ Five kinds of methods

3) Are these methods actually effective ?

→ Simulation by Labo. Cell

・Impurities additional Tests

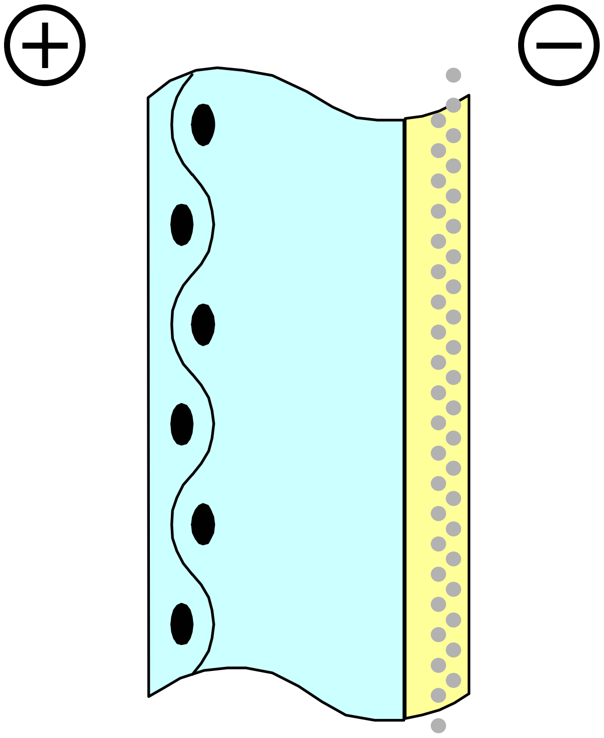
・Tests with membrane used by Customers

→ Examples of C.E. recovery in Commercial Plants

AGC Chemicals
Chemistry for a Blue Planet

AGC

Recovery Methods of Membrane Performance after Damaged by Impurities



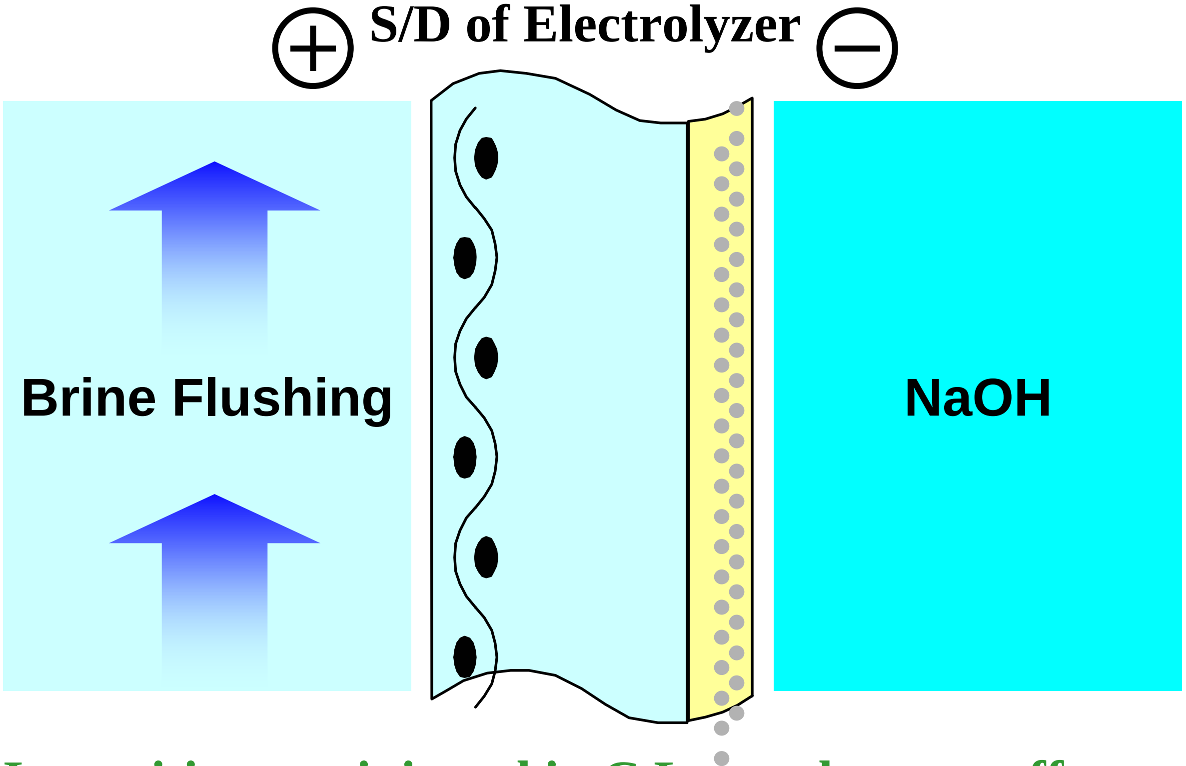
Methods

- **S/D of Electrolyzer**
  1. **Brine Flushing**
  2. **Water Flushing**
  3. **Treatment by Warm Water**

  (Ref.) Treatment by Acid

- **Operating**
  4. **Feed of Brine on Spec**
  5. **Low NaOH Conc.**

1. Brine Flushing



Impurities precipitated in C Layer does not effuse into Catolyte .⇒ less effective

Impurities in S Layer effuse into anolyte.
⇒ effective for Decrease in C.V.

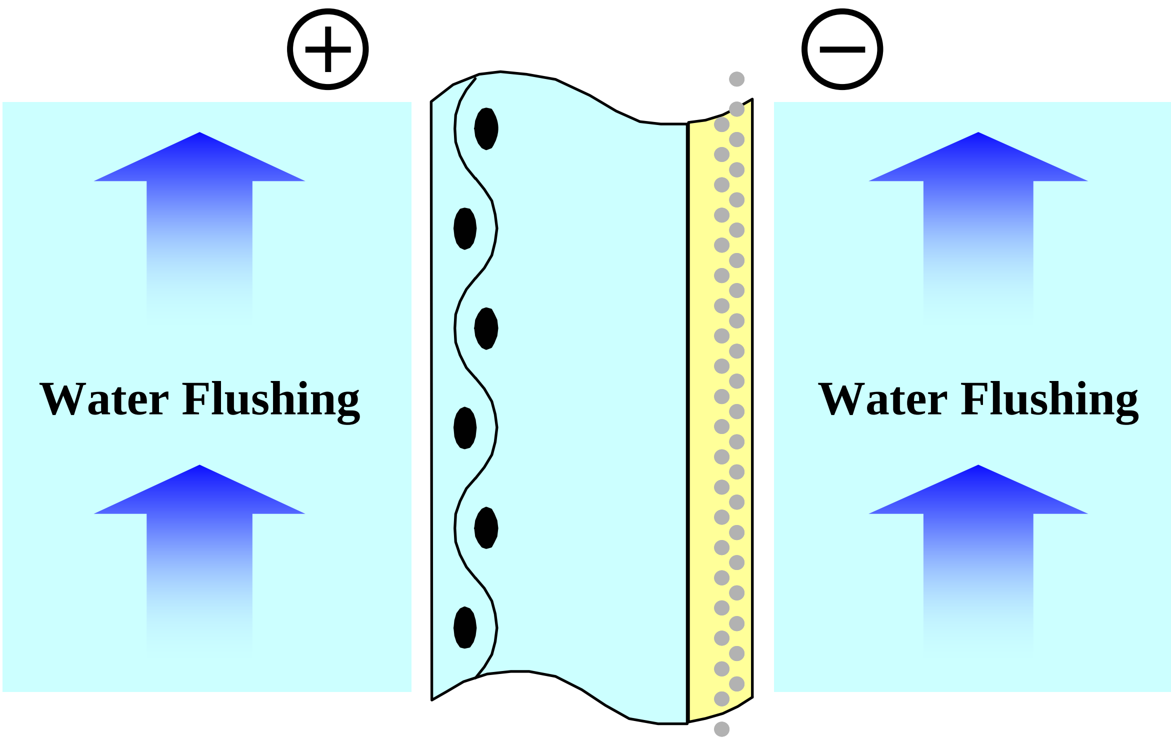
Methods

- **S/D of Electrolyzer**
  1. **Brine Flushing**
  2. Water Flushing
  3. Treatment by Warm Water

  (Ref.) Treatment by Acid
- Operating
  4. Feed of Brine on Spec
  5. Low NaOH Conc.

2. Water Flushing

S/D of Electrolyzer



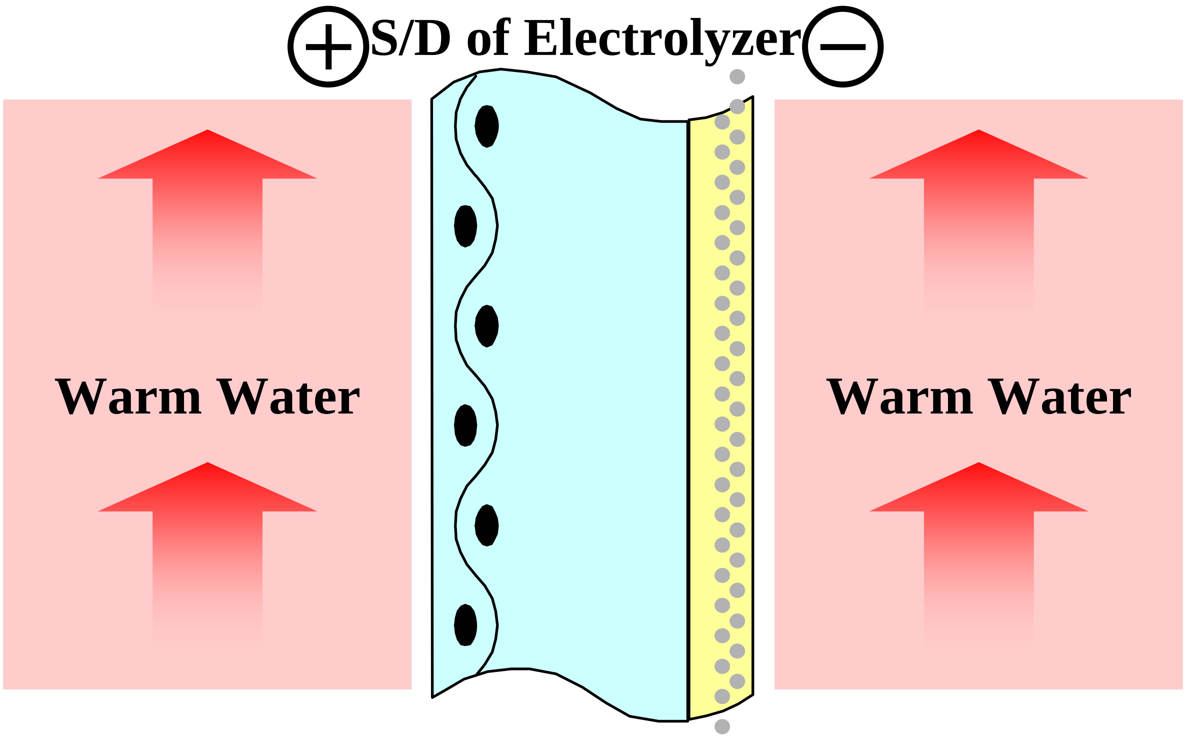
Effect by Water Flushing is moderate.

Methods

- S/D of Electrolyzer
  1. Brine Flushing
  2. Water Flushing
  3. Treatment by Warm Water

  (Ref.) Treatment by Acid
- Operating
  4. Feed of Brine on Spec
  5. Low NaOH Conc.

3. Treatment by Warm Water



Warm Water Treatment is effective for Effusion & Relax of dehydrated state

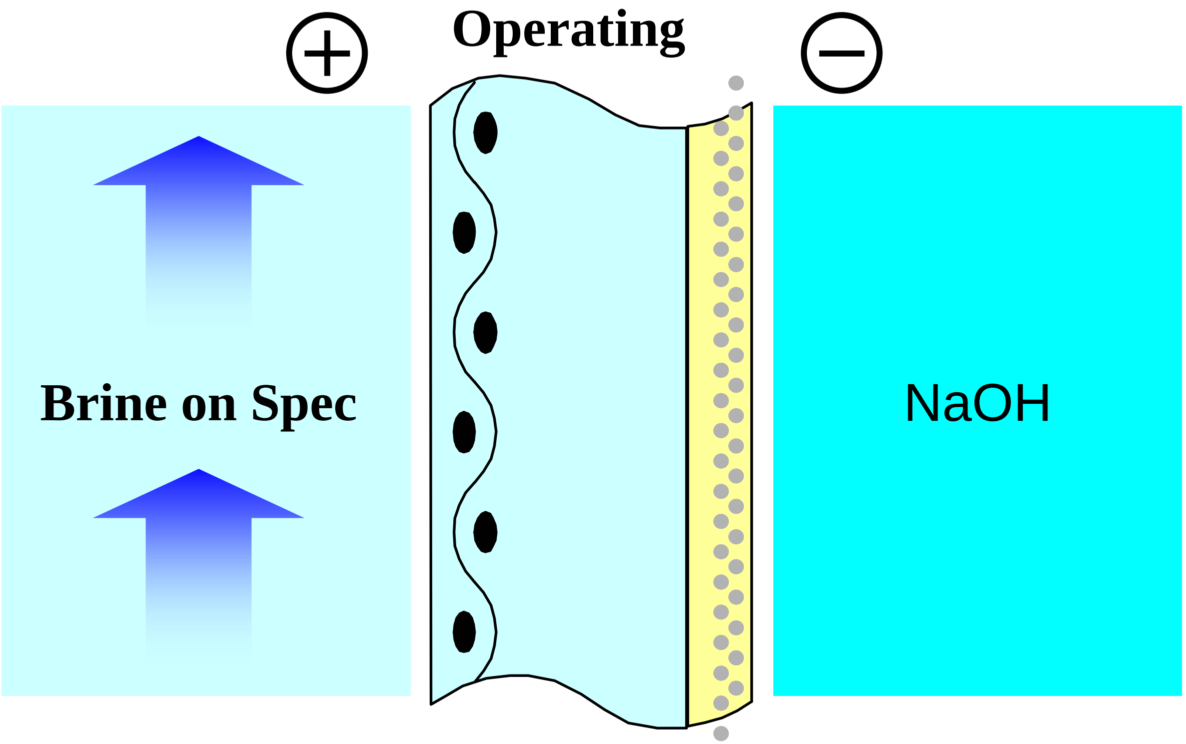
Methods

- **S/D of Electrolyzer**
  1. Brine Flushing
  2. Water Flushing
  3. **Treatment by Warm Water**

  (Ref.) Treatment by Acid

- Operating
  4. Feed of Brine on Spec
  5. Low NaOH Conc.

4. Feed of Brine on Specification in Operating

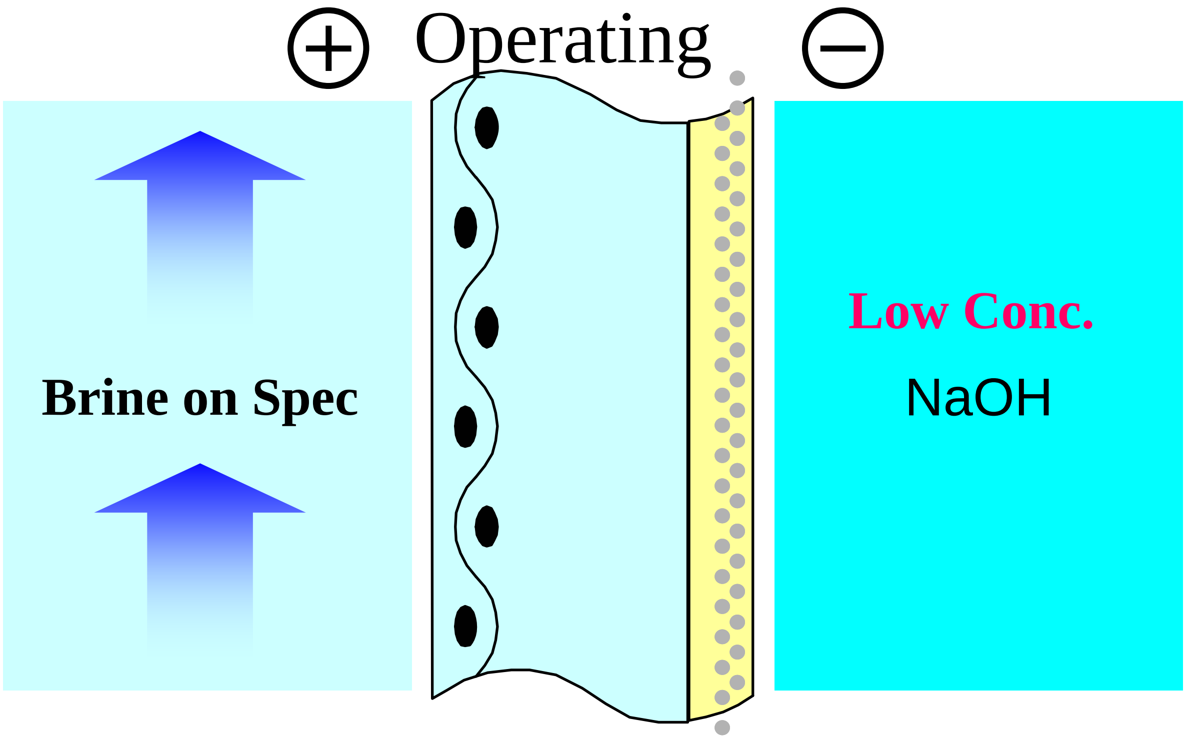


Methods

- S/D of Electrolyzer
  1. Brine Flushing
  2. Water Flushing
  3. Treatment by Warm Water
  (Ref.) Treatment by Acid
- Operating
  4. Feed of Brine on Spec
  5. Low NaOH Conc.

Effect by This Method is moderate

5. Operating under Low Concentration of NaOH



Methods

- S/D of Electrolyzer
  1. Brine Flushing
  2. Water Flushing
  3. Treatment by Warm Water

  (Ref.) Treatment by Acid

- **Operating**
  4. Feed of Brine on Spec
  5. **Low NaOH Conc.**

Low Conc. NaOH Operating is effective for Effusion & Relax from dehydrated state

Summary of Performance Recovery Method

Methods	Effect
• **S/D of Electrolyzer** 1. **Brine Flushing** 2. **Water Flushing** 3. **Treatment by Warm Water** **(Ref.) Treatment by Acid**	**Low** **High**
• **Operating** 4. **Feed of Brine on Spec** 5. **Low NaOH Conc.**	**Low** **High**

Summary of Performance Recovery Method

Methods	Condition（Example）	Effect
• **S/D of Electrolyzer**		Low
1. **Brine Flushing**	•R.T. 16Hrs *Some Effect of decrease in C.V.*	
2. **Water Flushing**	•R.T. 16Hrs	
3. **Treatment by Warm Water**	•50 degrees C 16Hrs	
(Ref.) Treatment by Acid	*Never Applicable* •1N-HCl → 1N-NaOH → Warm Water	High
• **Operating**		Low
4. **Feed of Brine on Spec**		
5. **Low NaOH Conc.**	･**25% NaOH Operating**	High

These Condition are dependent on each Customer's situation.

Summary of Performance Recovery Method

Methods	Condition (Example)	Effect
• **S/D of Electrolyzer**		Low
1. Brine Flushing	•R.T. 16Hrs *(Some Effect of decrease in C.V.)*	
2. Water Flushing	•R.T. 16Hrs	
3. Treatment by Warm Water	•50 degrees C 16Hrs	
(Ref.) Treatment by Acid	•1N-HCl → 1N-NaOH → Warm Water *(Never Applicable)*	High
• **Operating**		Low
4. Feed of Brine on Spec		
5. Low NaOH Conc.	▪**25% NaOH Operating**	High

AGC recommends 3 kinds of Recovery Methods.

Summary of Performance Recovery Method

Methods

- **S/D of Electrolyzer**
  1. **Brine Flushing**
  2. **Water Flushing**
  3. **Treatment by Warm Water**

  (Ref.) Treatment by Acid

- **Operating**
  4. **Feed of Brine on Spec**
  5. **Low NaOH Conc.**

More effective condition

1) Preferable PH is around 6-8

2) Higher Temp. is preferable
(Actually 50-70 degrees C)

We should consider Working Efficiency.

Q: Does C.E. recover after damaged by Impurity ?

1) What affects the recovery of C.E.?

→" Model of Impurities Precipitation"

2) What are the methods for recovery ?

→ Five kinds of methods

3) Are these methods actually effective ?

→ Simulation by Labo. Cell

・Impurities additional Tests

・Tests with membrane used by Customers

→ Examples of C.E. recovery
in Commercial Plants

Simulation Tests of C.E. Recovery by Labo. Cell

Methods	Condition (Example)	Effect
• **S/D of Electrolyzer**	Some Effect of decrease in C.V.	Low
1. **Brine Flushing**	•R.T. 16Hrs	
2. **Water Flushing**	•R.T. 16Hrs	
3. **Treatment by Warm Water**	•50 degrees C 16Hrs	
(Ref.) Treatment by Acid	Never Applicable •1N-HCl → 1N-NaOH → Warm Water	High
• **Operating**		Low
4. **Feed of Brine on Spec**		
5. **Low NaOH Conc.**	･25% NaOH Operating	High

Here 3 kinds of recovery method are chosen.

Evaluation Condition for Simulation tests

Impurities	Content	Time in Adding	Membrane
1. I/Ba	10 / 1ppm	14 days	F892
2. Sr	1ppm	14 days	F8935
3. Ca	0.1～0.2ppm	30 days	F8935
4. Al/SiO_2	0.5 / 3～4ppm	37 days	F8935
5. Ca/SiO_2	0.2 / 15ppm	19 days	F8020

3 kinds of recovery method will be carried out after above adding term.

Remark: Acid treatment can't be applied to commercial plants.

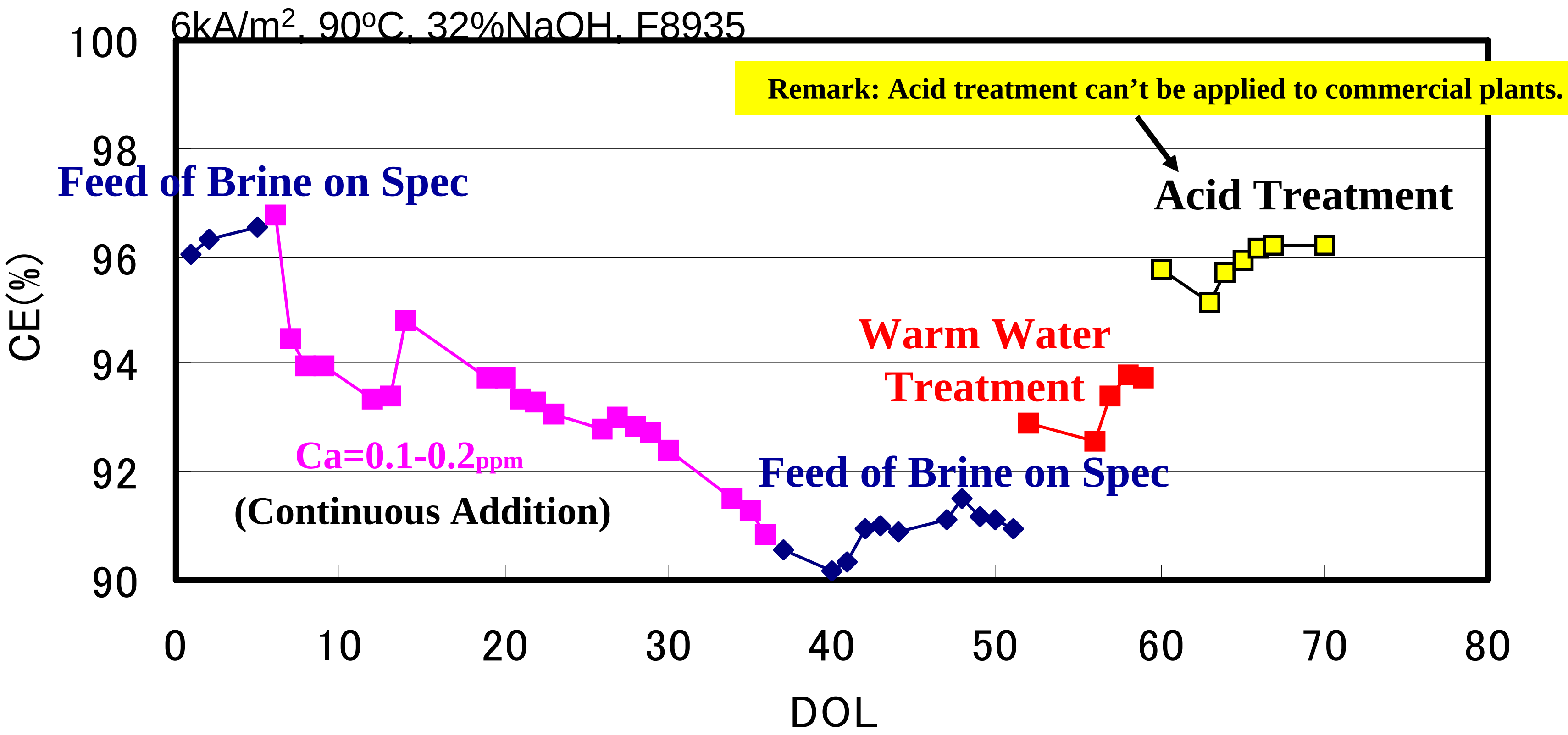
Evaluation Condition for Simulation tests

Impurities	Content	Time in Adding	Membrane
1. I/Ba	10 / 1ppm	14 days	F892
2. Sr	1ppm	14 days	F8935
3. Ca	0.1～0.2ppm	30 days	F8935
4. Al/SiO_2	0.5 / 3～4ppm	37 days	F8935
5. Ca/SiO_2	0.2 / 15ppm	19 days	F8020

3 kinds of recovery method will be carried out after above adding term.

Remark: Acid treatment can't be applied to commercial plants.

3. Ca=0.1-0.2ppm



	Brine on Spec	Warm Water	Acid
3. Ca	★	★★	★★★

Characteristic of C.E. Recovery after Damaged by Ca Impurity

	Brine on Spec	Warm Water	Acid	
1. I/Ba				
2. Sr				
3. Ca	★	★★	★★★	
4. Al/SiO_2				
5. Ca/SiO_2				

Similarly , Results regarding Other Impurities are …….

AGC Chemicals
Chemistry for a Blue Planet

AGC

Characteristic of C.E. Recovery after Damaged by Some Impurities

	Brine on Spec	Warm Water	Acid	Recovery
1. I/Ba	★★	★★★	★★★	High
2. Sr	★★	★★	★★★	
3. Ca	★	★★	★★★	
4. Al/SiO_2	★	★★	★★★	
5. Ca/SiO_2	★	★	★★	Low

Characteristics of C.E. Recovery differs variously among Impurities.

What does C.E. Recovery depend on ?

What does C.E. Recovery depend on ?

1. C.E. Recovery depends on the kinds of damage.
2. Damage depends on the size of Particles in the surface layer of C-layer.

*** Key Points for Recovery are

1) Effusion of Impurities from C-Layer
2) Relax from dehydrated state in C-Layer

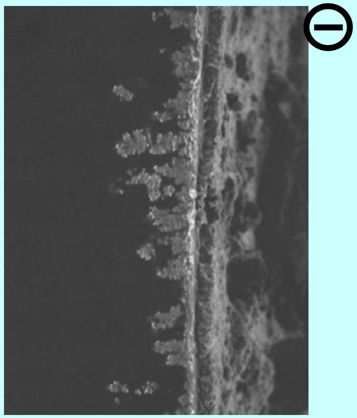
Characteristic of C.E. Recovery after Damaged by Some Impurities

	Brine on Spec	Warm Water	Acid	Recovery
1. I/Ba	★★	★★★	★★★	High
2. Sr	★★	★★	★★★	
3. Ca	★	★★	★★★	
4. Al/SiO_2	★	★★	★★★	
5. Ca/SiO_2	★	★	★★	Low

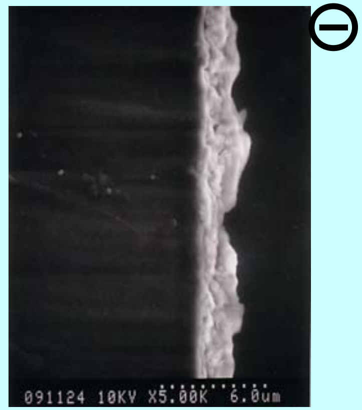
Correlation between Recovery by Brine on Spec & Particle's Size?

Correlation

between Recovery by Brine on Spec & Particle's Size



I/Ba



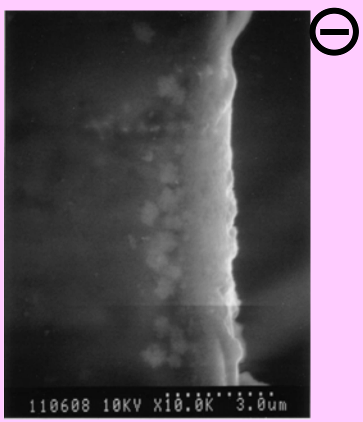
Sr

Fine Particle or Invisible

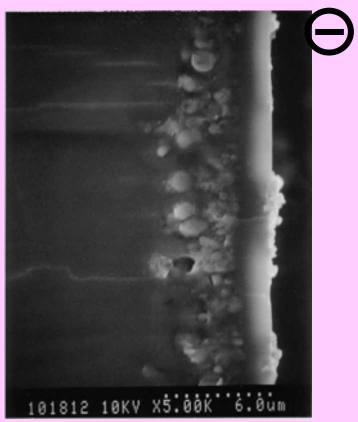
↓

Moderate Recovery

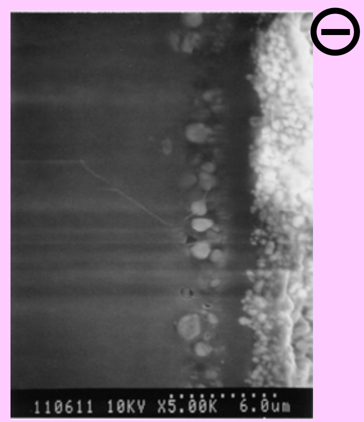
★★



Ca



Al/SiO_2



Ca/SiO_2

Middle / Large Particles

↓

Less Recovery

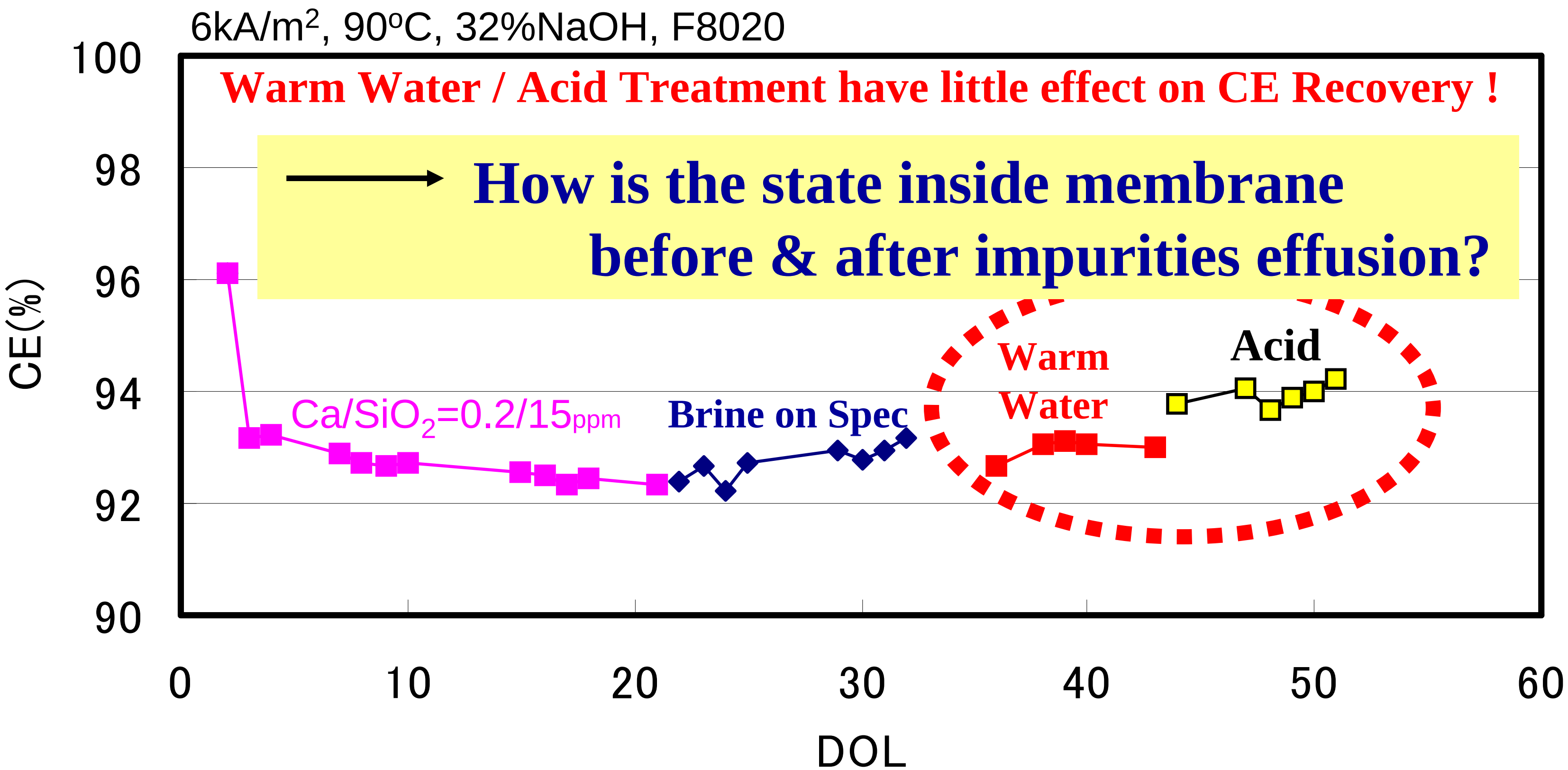
★

Characteristic of C.E. Recovery after Damaged by Some Impurities

	Brine on Spec	Warm Water	Acid	Particle Size
1. I/Ba	★★	★★★	★★★	Fine
2. Sr	★★	★★	★★★	Invisible
3. Ca	★	★★	★★★	Middle
4. Al/SiO_2	★	★★	★★★	Large
5. Ca/SiO_2	★	★	★★	Large

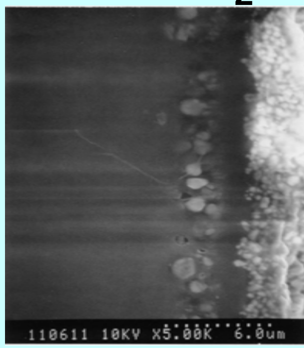
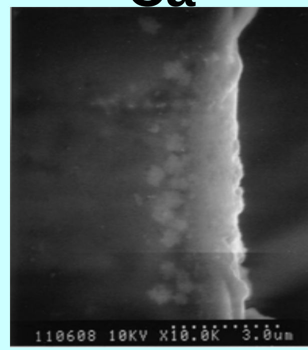
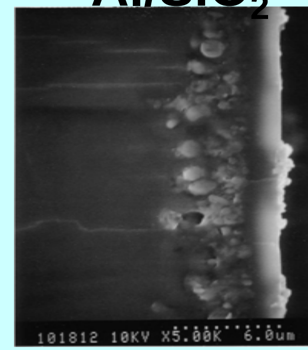
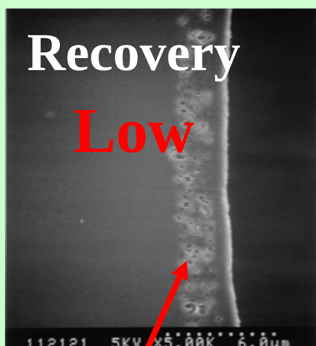
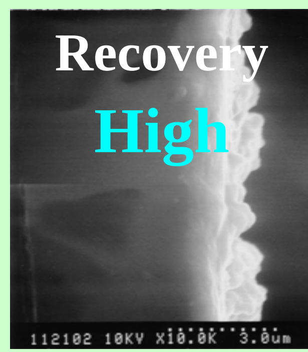
<u>Particle Size affects C.E. Recovery by Brine on Spec.</u>

6. Ca/SiO_2=0.2/15ppm at 6kA/m^2



	Brine on Spec	Warm Water	Acid
6. Ca/SiO2	★	★	★★

Membrane before & after Impurities Effusion

	Ca/SiO_2	Ca	Al/SiO_2
Before			
After			
	Voids	Invisible	Invisible

AGC Chemicals
Chemistry for a Blue Planet

AGC

Characteristic of C.E. Recovery after Impurities Effusion

	Brine on Spec	Warm Water	Acid	Voids
1. I/Ba	★★	★★★	★★★	
2. Sr	★★	★★	★★★	
3. Ca	★	★★	★★★	Invisible
4. Al/SiO_2	★	★★	★★★	Invisible
5. Ca/SiO_2	★	★	★★	Visible

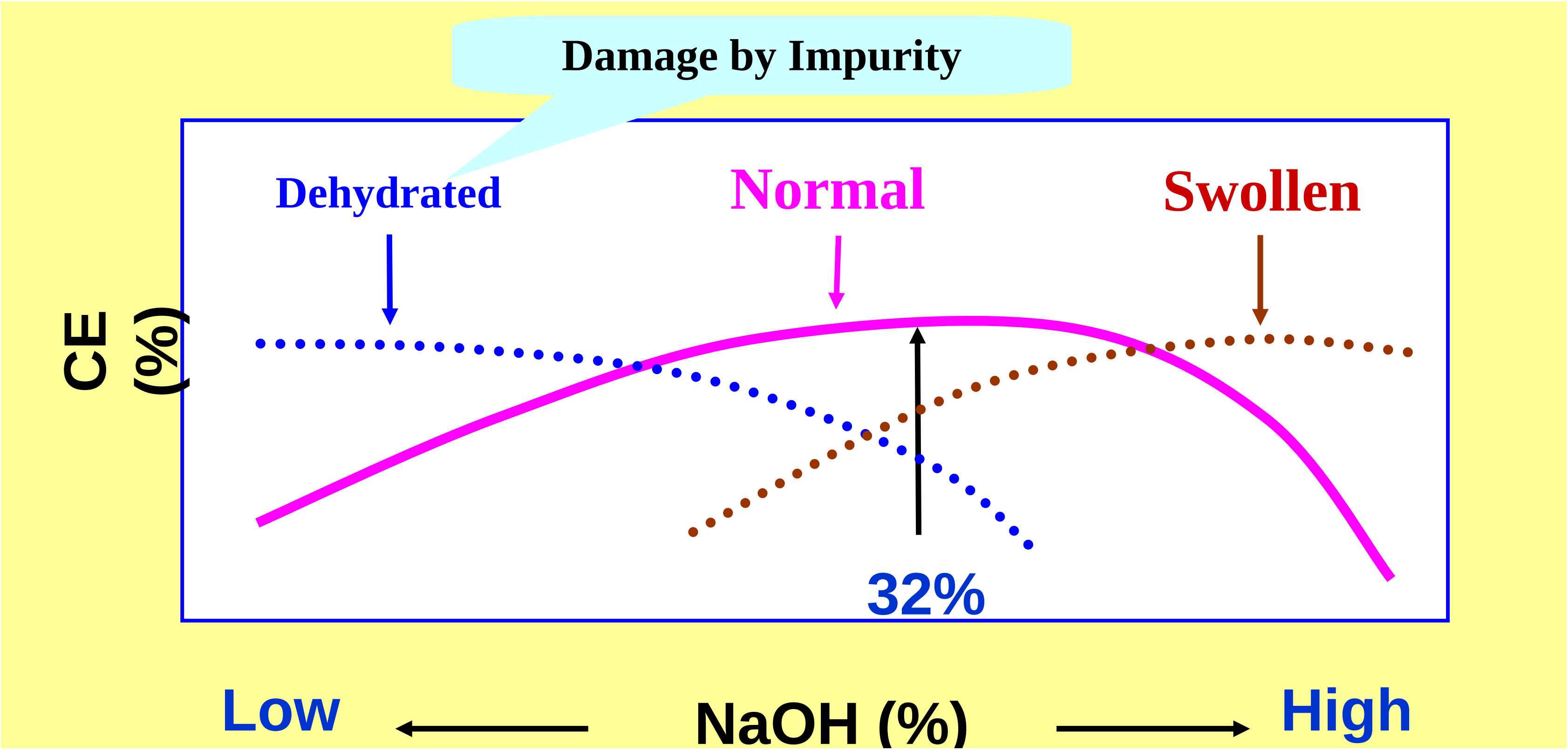
CE Recovery after Effusion depends on the degree of Polymer Destruction

Summary of Performance Recovery Method

Methods	Condition（Example）	Effect
• **S/D of Electrolyzer**		Low
1．**Brine Flushing**	•R.T. 16Hrs	
2．**Water Flushing**	•R.T. 16Hrs	
3．**Treatment by Warm Water**	•50 degrees C 16Hrs	
(Ref.) Treatment by Acid	•1N-HCl → 1N-NaOH → Warm Water (Never Applicable)	High
• **Operating**		Low
4．**Feed of Brine on Spec**		
5 **Low NaOH Conc.**	･**25% NaOH Operating**	High

Q: Why does Low NaOH Conc. have high effect ?

Effect of NaOH Conc. on C.E. & Membrane State



Membrane after damaged often recovers under Low NaOH Conc. Operating.

Q: Does C.E. recover after damaged by Impurity ?

1) What affects the recovery of C.E.?

→" Model of Impurities Precipitation"

2) What are the methods for recovery ?

→ Five kinds of methods

3) Are these methods actually effective ?

→ Simulation by Labo. Cell

・Impurities additional Tests

・Tests with membrane used by Customers

→ Examples of C.E. recovery

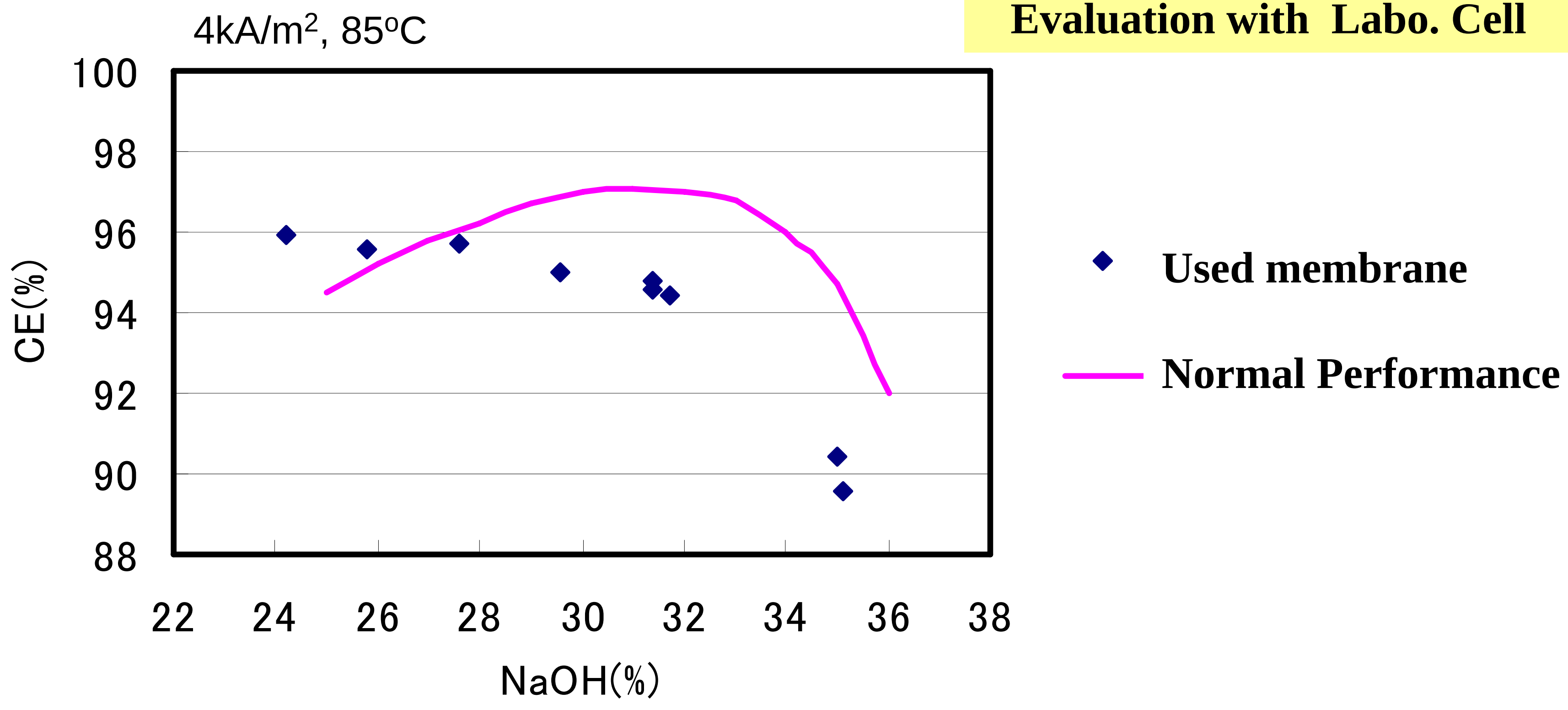
in Commercial Plants

AGC Chemicals
Chemistry for a Blue Planet

AGC

CE Recovery by Warm Water Treatment Company A

Evaluation with Labo. Cell

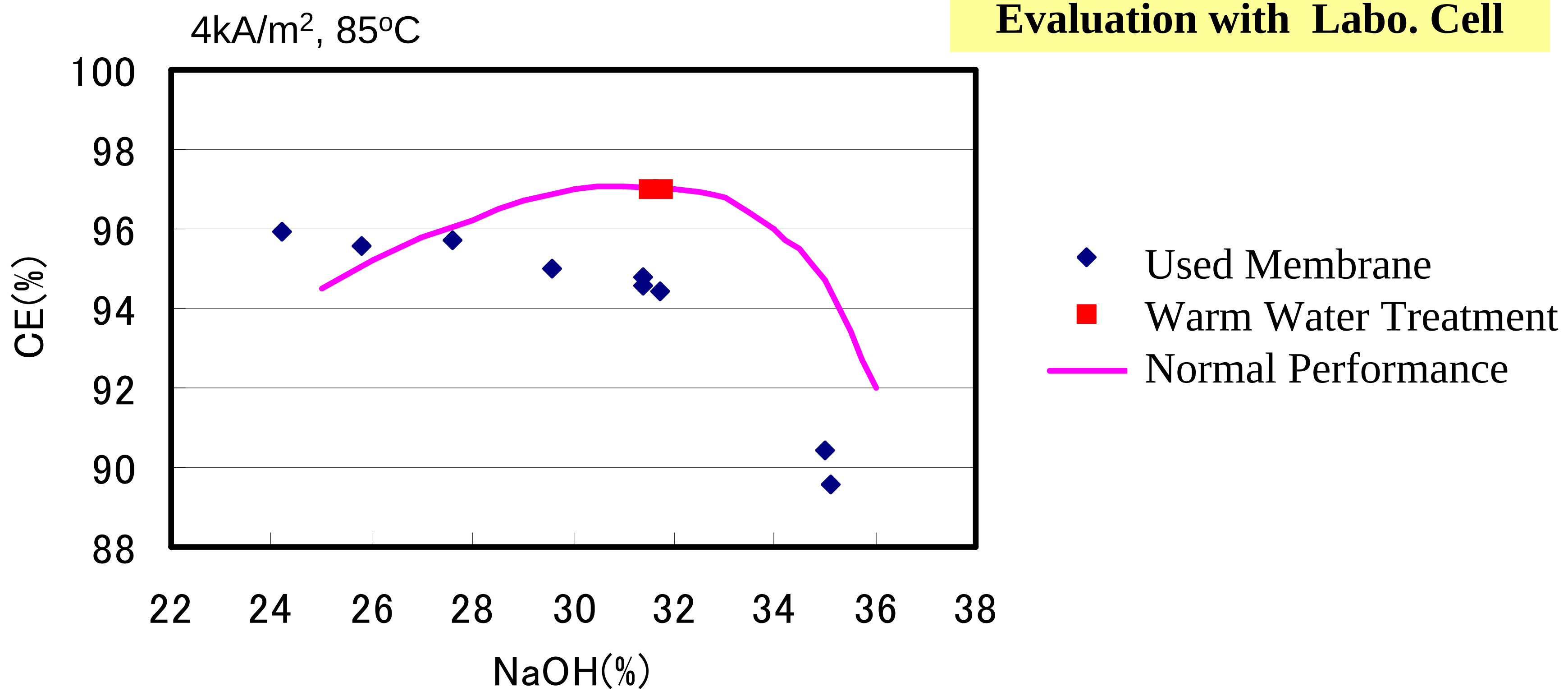


Membrane after damaged often recovers under Low NaOH Conc. Operating.

AGC Chemicals
Chemistry for a Blue Planet

CE Recovery by Warm Water Treatment Company A

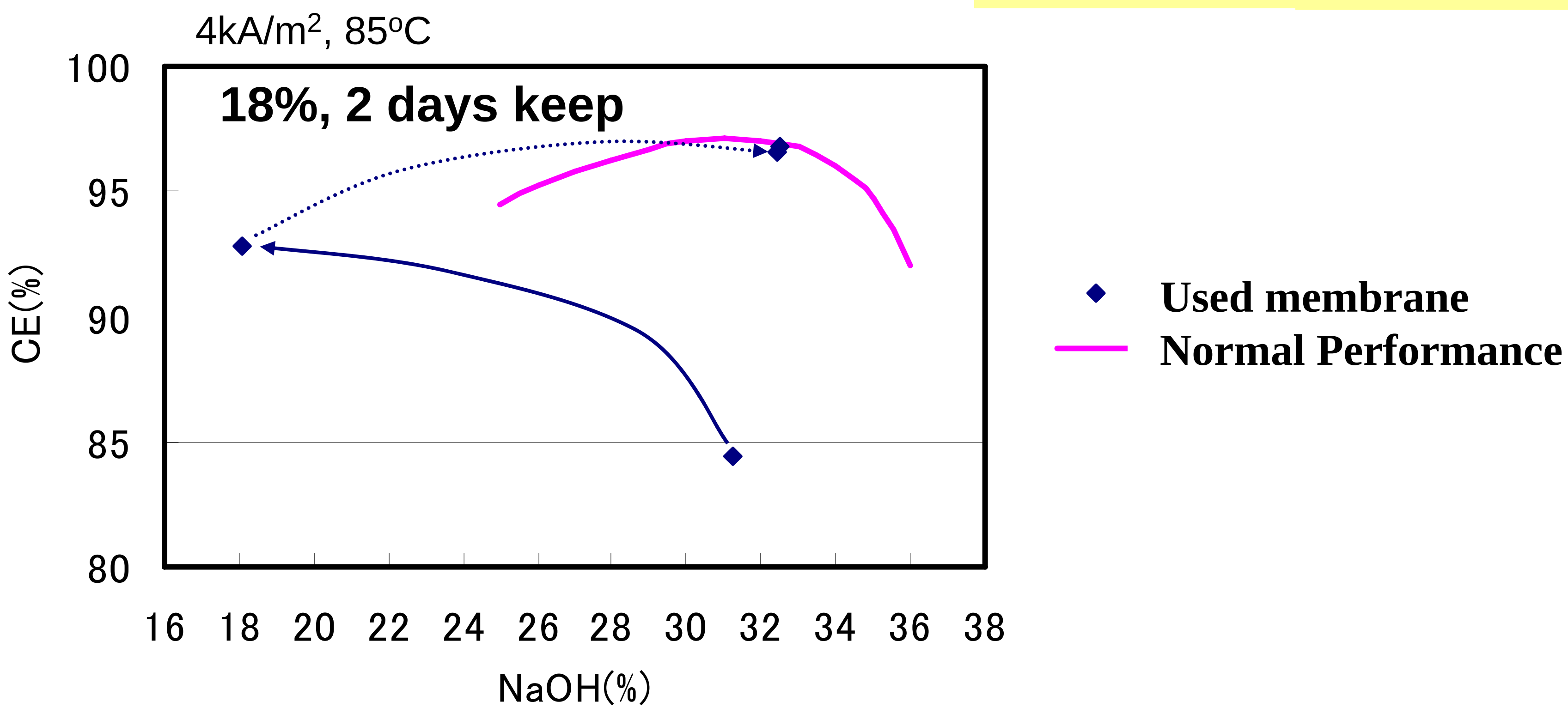
Evaluation with Labo. Cell



<u>CE of Used Membrane Recovered by Warm Water almost up to Original Performance</u>

CE Recovery by Low NaOH Conc. Operating Company B

Evaluation with Labo. Cell



This Method often has High Effect.

However We should Consider Productivity of Plants.

Q: Does C.E. recover after damaged by Impurity ?

1) What affects the recovery of C.E.?

→" Model of Impurities Precipitation"

2) What are the methods for recovery ?

→ Five kinds of methods

3) Are these methods actually effective ?

→ Simulation by Labo. Cell

・Impurities additional Tests

・Tests with membrane used by Customers

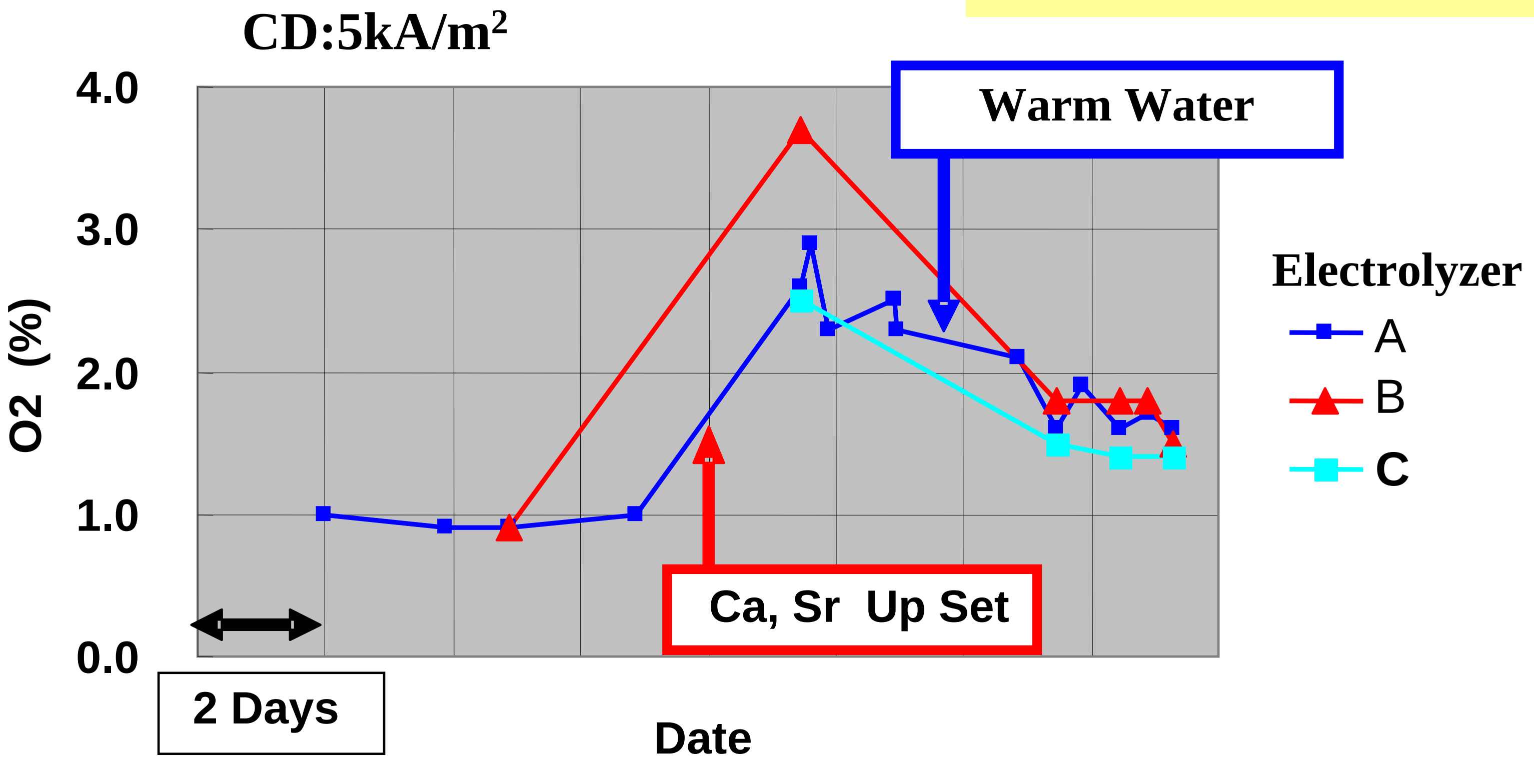
→ Examples of C.E. recovery in Commercial Plants

AGC Chemicals
Chemistry for a Blue Planet

AGC

Recovery of CE by Warm Water after Ca,Sr Damage

In a Actual Commercial Plant
"C"

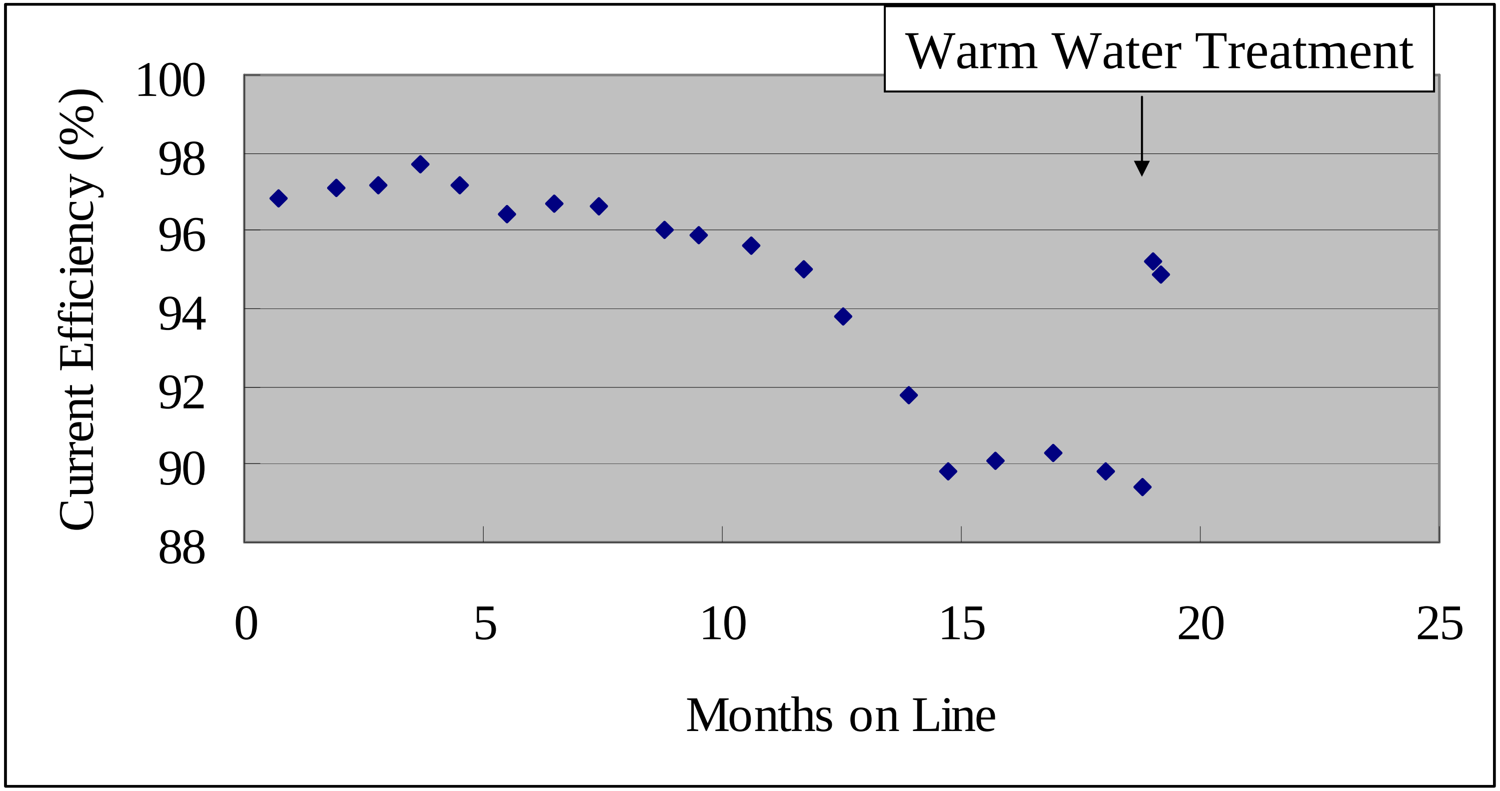


AGC Chemicals
Chemistry for a Blue Planet

Recovery of CE by Warm Water after I / Ba Damage

Plant, 3.8kA/m^2, F-8934

In a Real Commercial Plant "D"



AGC Chemicals
Chemistry for a Blue Planet

AGC

Recent Other Examples of Recovery of CE by Water Flushing after Some Damages

In Some Real Commercial Plants

Company	Damage	Results
E	Ca, Sr	CE 91% → more than 94%
F	Ca, Sr	CE 85% → more than95%
G	Organics?	We received information regarding CE recovery

Conclusion until now

Q: Does C.E. recover after damaged by Impurity ?

After damaged by Impurities, CE doesn't always recover completely!

1) What does C.E. Recovery depend on ?

- **C.E. Recovery depends on the kinds of damage.**
- **Damage depends on the size of Particles in the surface layer of C-layer.**

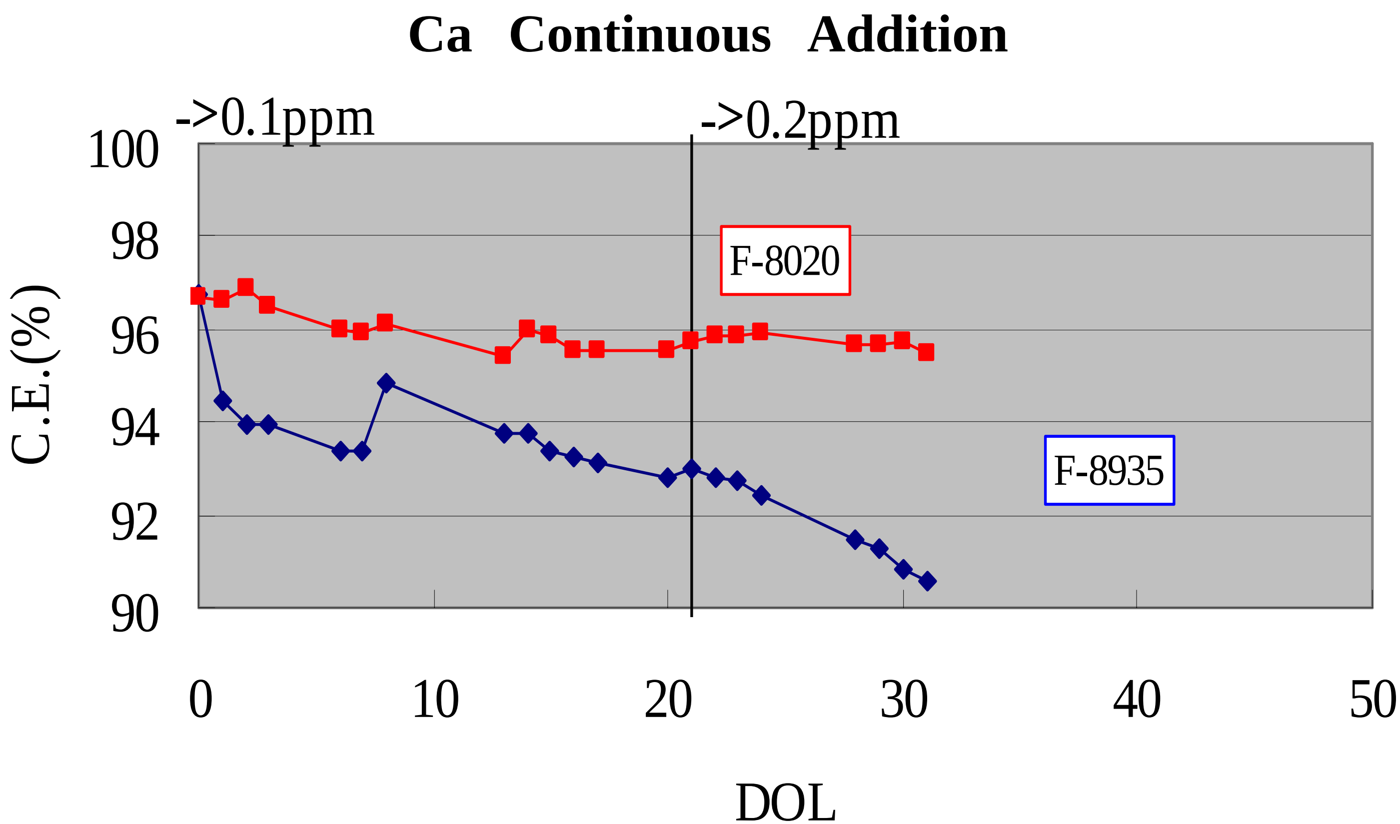
2) What are the method for performance recovery if damage by impurities should occur?

We propose

- **Water Flushing**
- **Warm Water Treatment**
- **Operating under Low NaOH Conc. , if possible.**

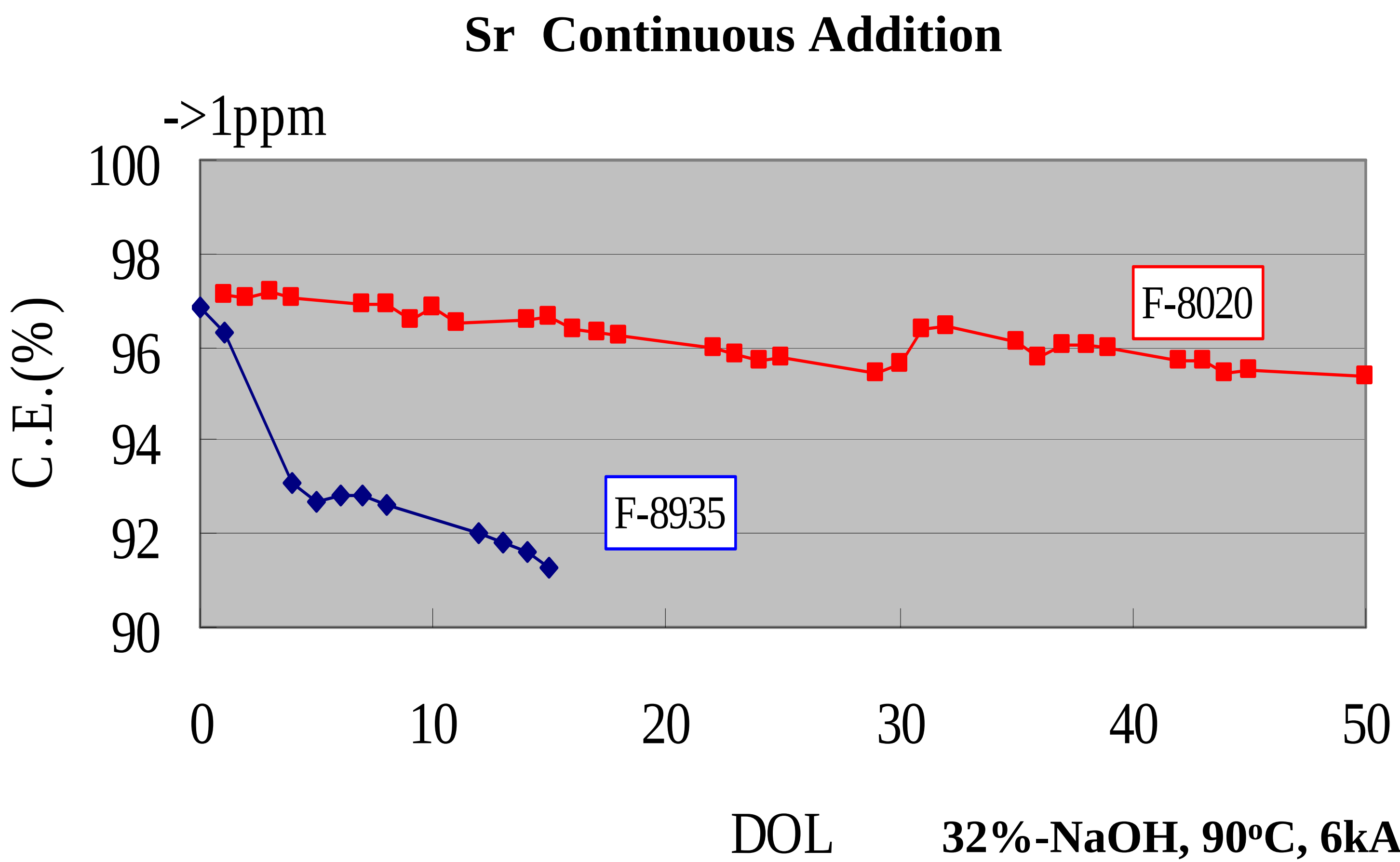
→ **We expect CE recovery by 2 - 5%**

Durability of F-8020 against Ca in Brine



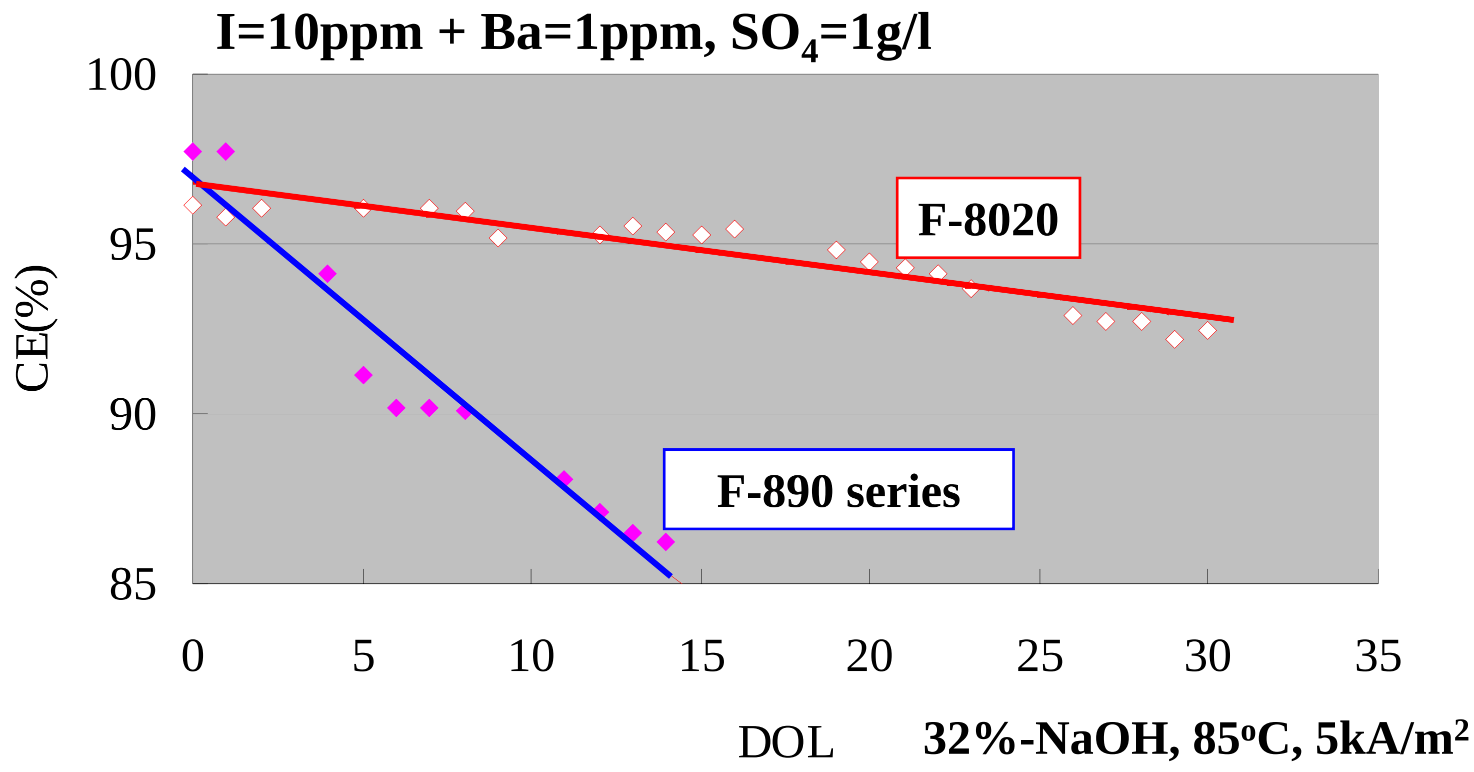
32%-NaOH, 90°C, 6 kA/m²

Durability of F-8020 against Sr in Brine

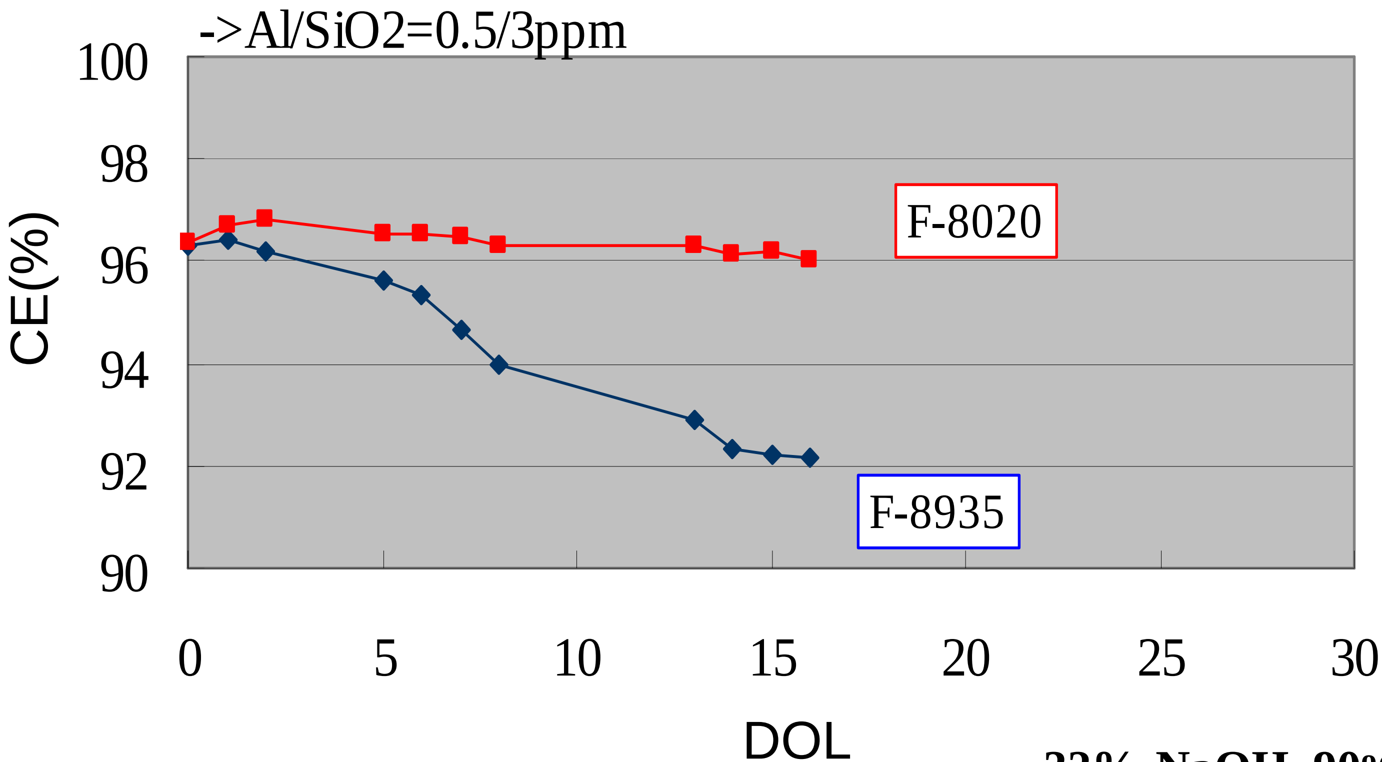


32%-NaOH, 90^{o}C, 6kA/m^2

Durability of F-8020 against I/Ba in Brine



Durability of F-8020 against Al/SiO2 in Brine



32%-NaOH, 90^{o}C, 6 kA/m^2

Procedure of Countermeasure after damaged by Impurities

1) **Shut Down as soon as possible**

2) **Discharge all electrolyte in the electrolyzer**

3) **Carry out water flushing or warm water treatment**

(Preferable condition is 60 degree-C, more than 16 hrs.)

<u>Following is preferable to carry out after consideration of productivity .</u>

4) Strat up at 25% NaOH Conc.

5) Operating under 25-28% NaOH for 2-5 days

Today Presentation consists of

1. Model of Membrane Damage by Impurities
2. Introduction of C.E. Recovery Methods
3. Verification of Effects by these Methods with Labo. Cell & Commercial Plants
4. Durability of F8020 against Impurities
5. **Introduction of F8020SP**

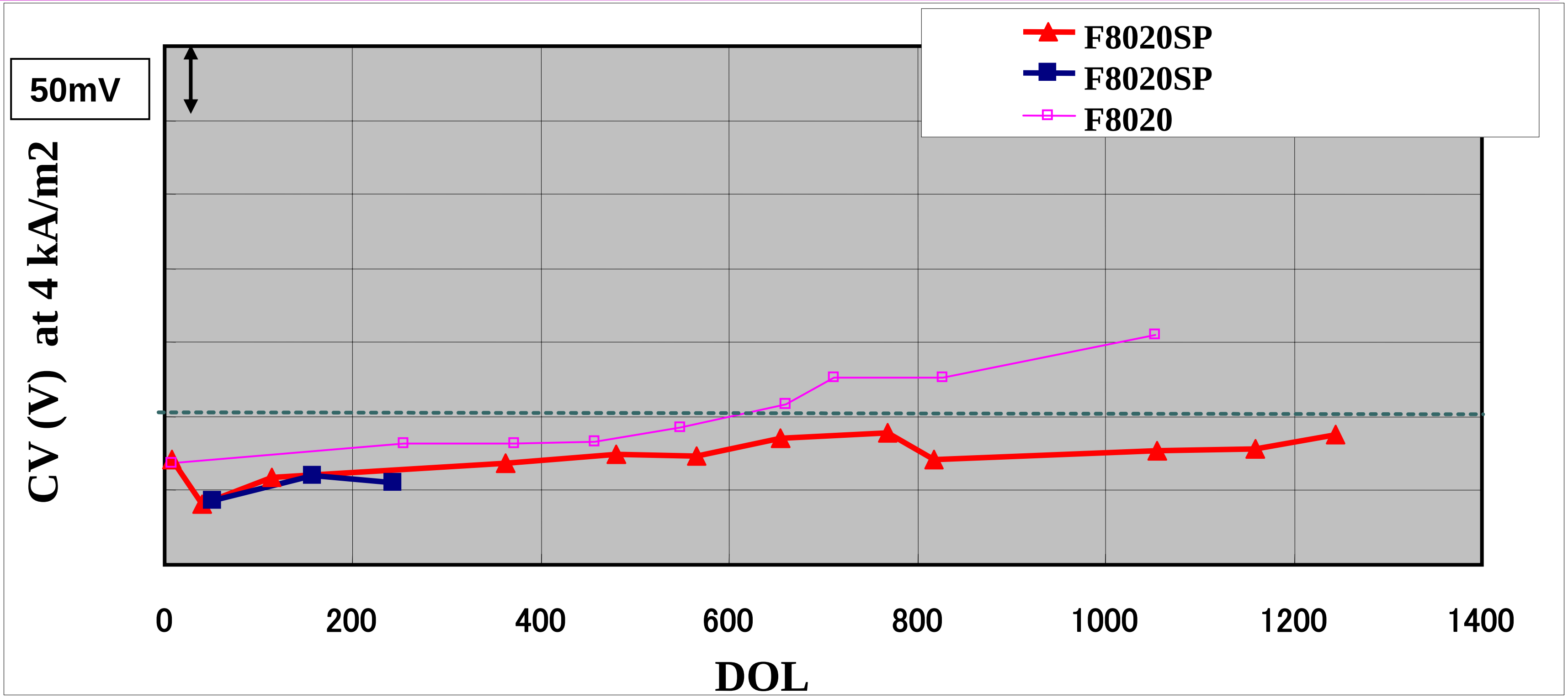
Enhanced Feature of F8020SP compared with F8020

1. **Wider Operation Range (NaOH conc. vs. CE)**
2. **20~30 mV lower Voltage at 6 kA/m^2**
3. **Voltage stability**
4. **Higher Durability against Iodine/Alkali Earth Metal**
5. **Higher Durability in Cl_2 Gas Stagnation-Zone**
6. **Extended Performance Characteristics for higher Current Density Operation**
7. **Higher Mechanical Strength**

Enhanced Feature of F8020SP compared with F8020

1. Wider Operation Range (NaOH conc. vs. CE)
2. 20~30 mV lower Voltage at 6 KA/m^2
3. Voltage stability
4. Higher Durability against Iodine/Alkali Earth Metal
5. Higher Durability in Cl_2 Gas Stagnation-Zone
6. Extended Performance Characteristics for higher Current Density Operation
7. Higher Mechanical Strength

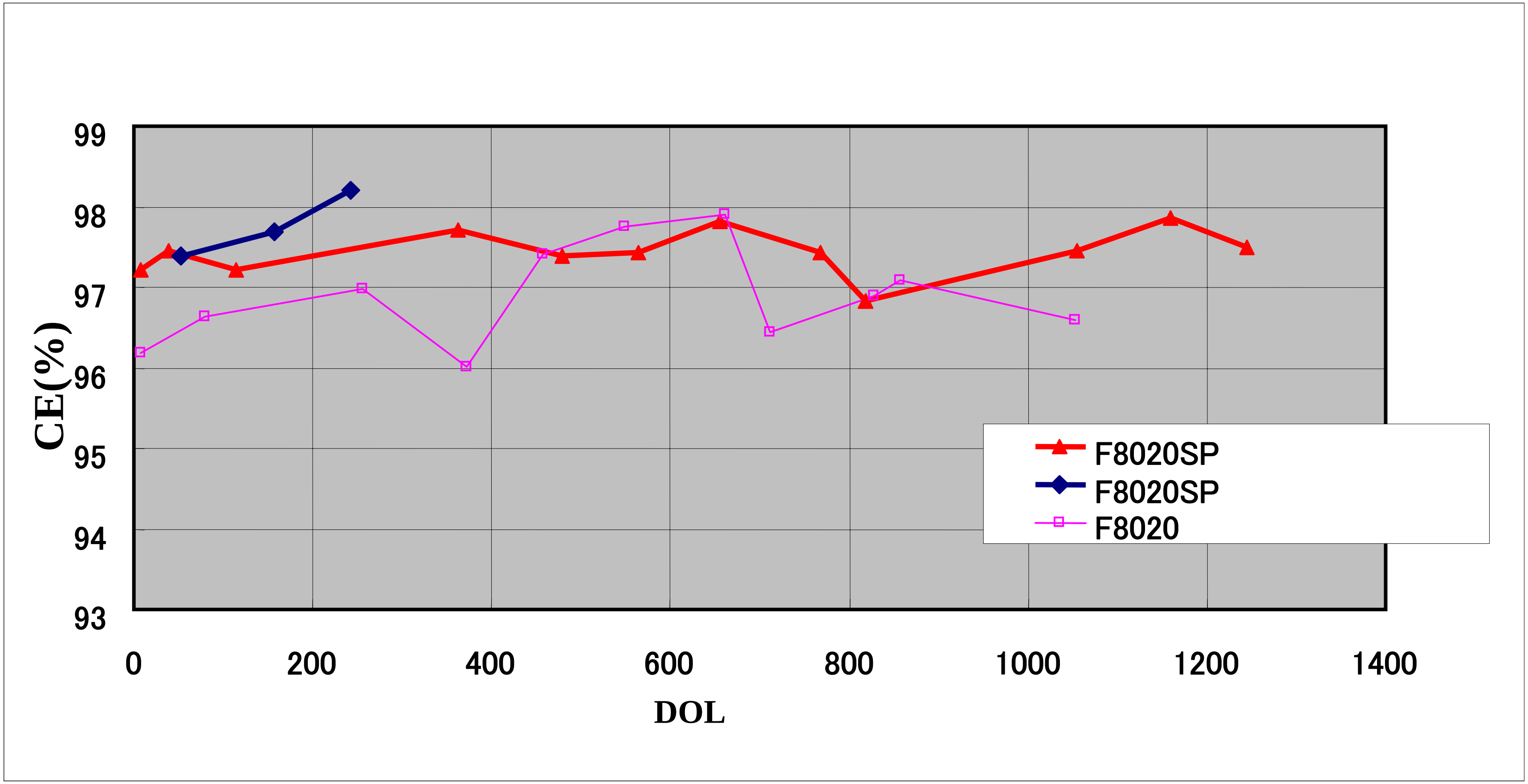
AGC Chiba Factory F8020SP CV (M3 Cell)



F8020SP has been operated more than 3 years in AGC factory.

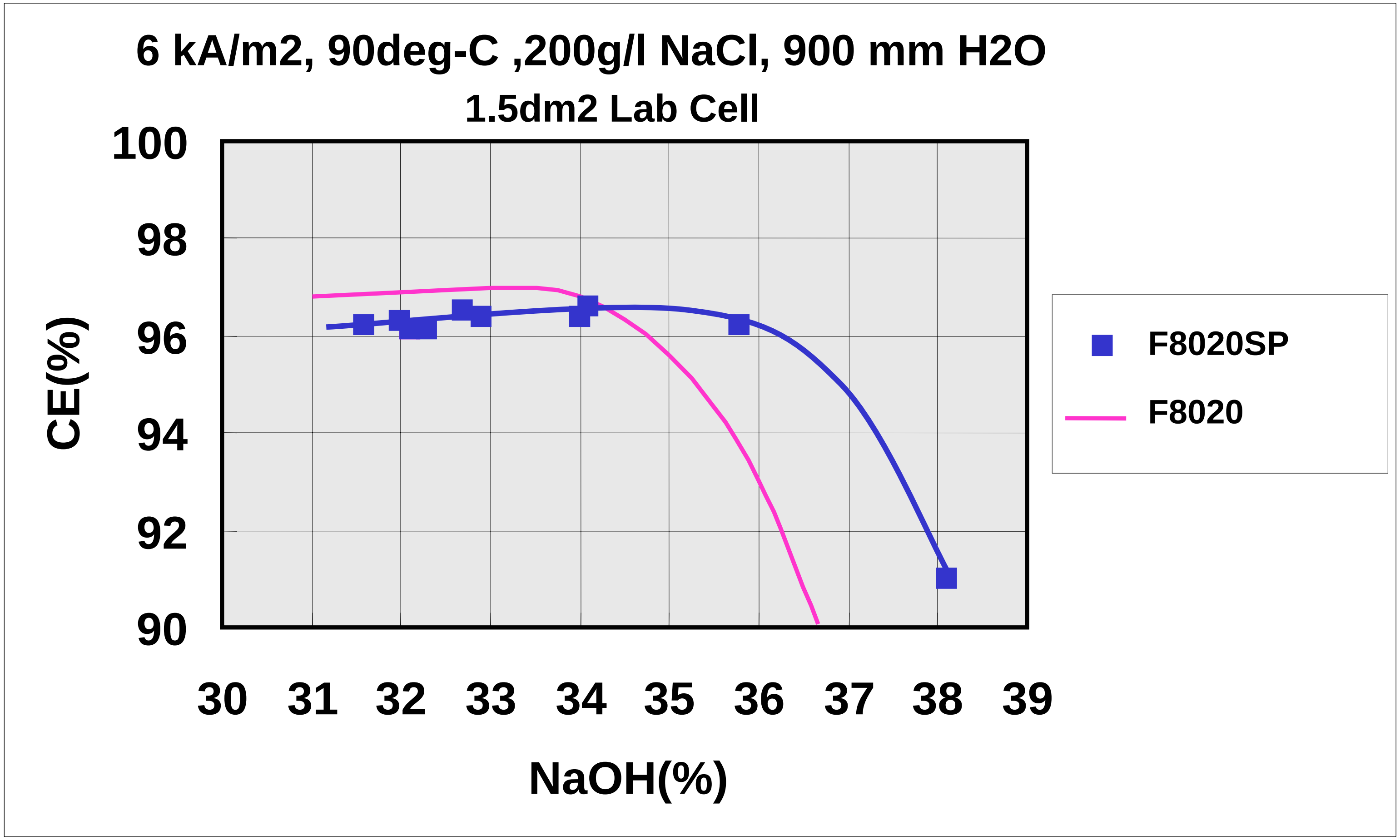
F8020SP keeps more stable voltage than F8020

AGC Chiba Factory F8020SP CE



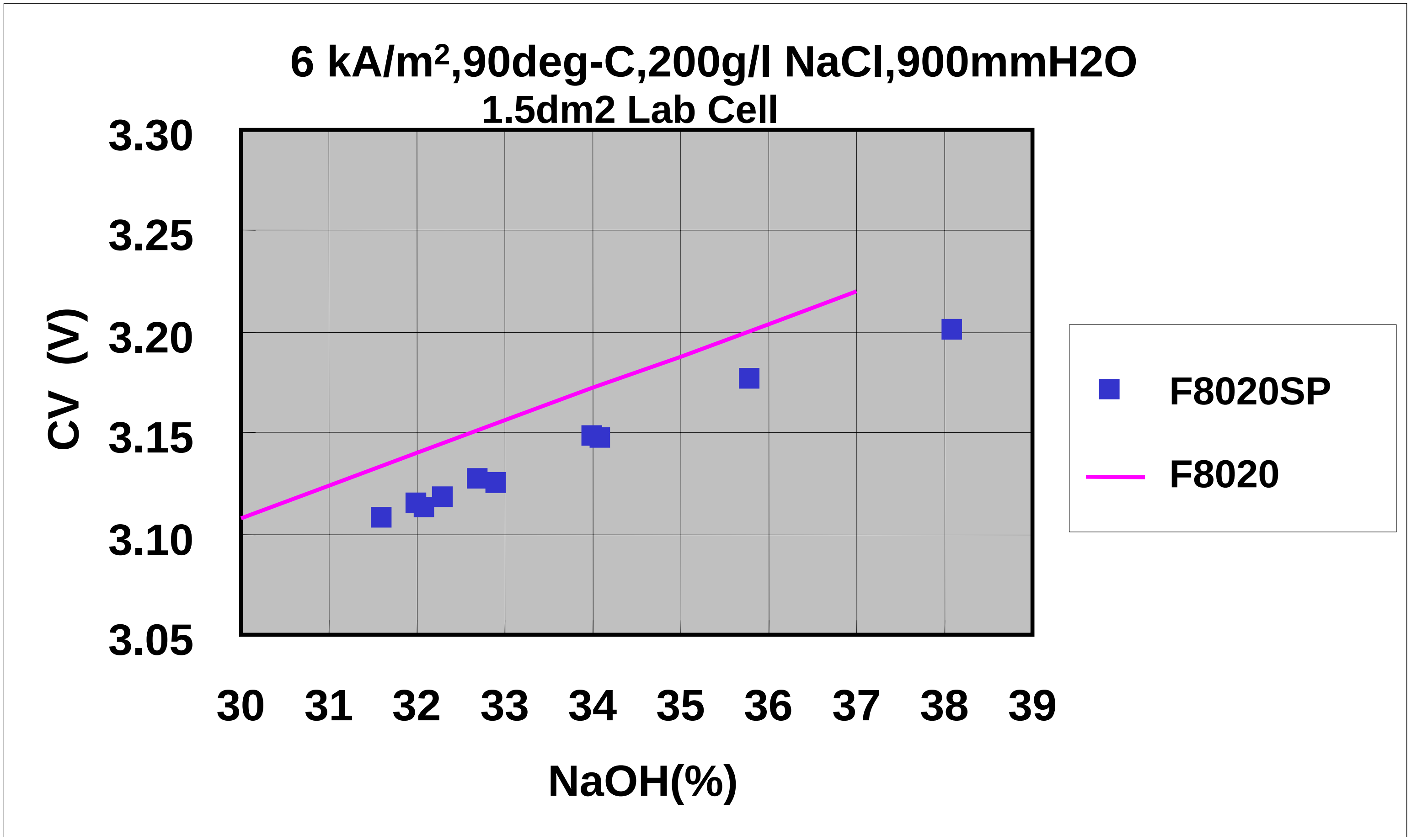
F8020SP keeps higher and more stable Current Efficiency than F8020

CE Curves of F8020SP in Lab. Cell



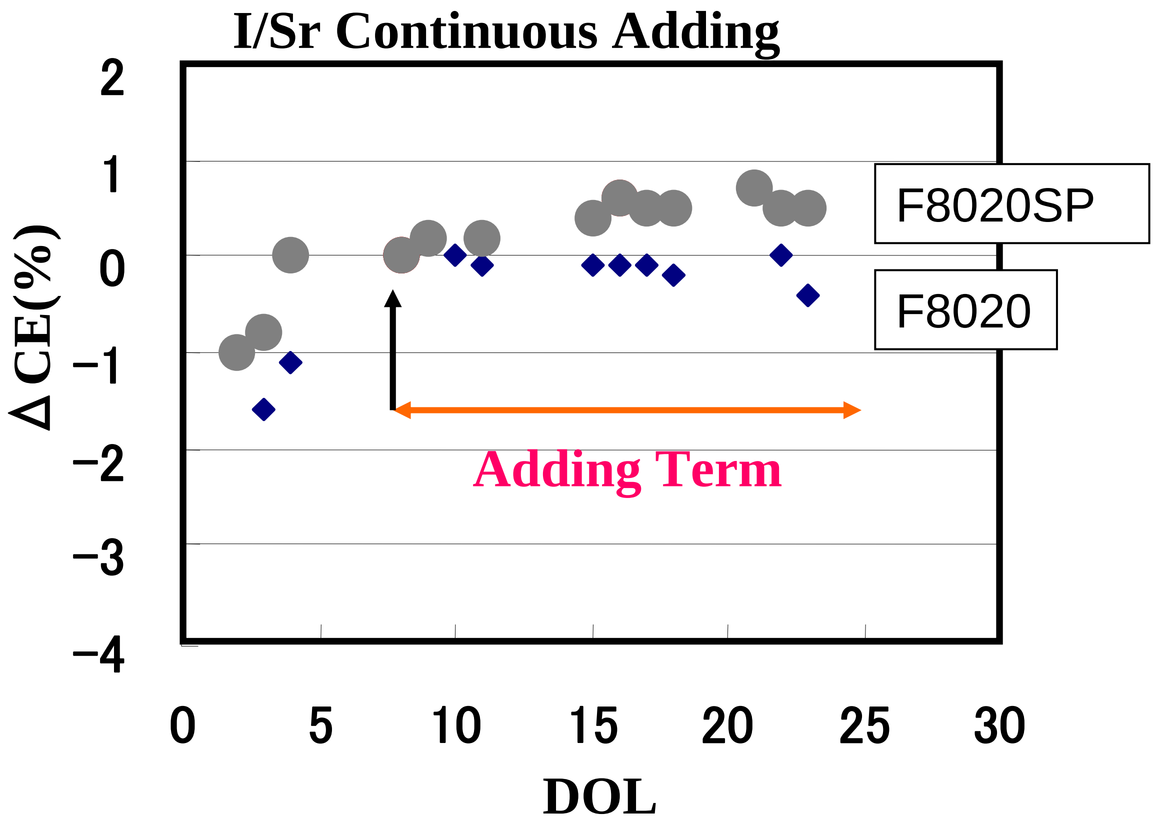
F8020SP has wider Operating Range than F8020

Voltage of F8020SP



F8020SP shows lower voltage than F8020

I/Sr Addition (I/Sr = 20/1 ppm at 6 kA/m^2)



F8020SP keeps good performance even after I/Sr addition compared with F8020.


Thank you for your attention