



*2006 Symposium of
The Korean Institute of Chemical Engineers*

***Purification of phosphoric acid from the waste
acids in LCD manufacturing process***

2006. 4. 21



Daeil Development Co., Ltd



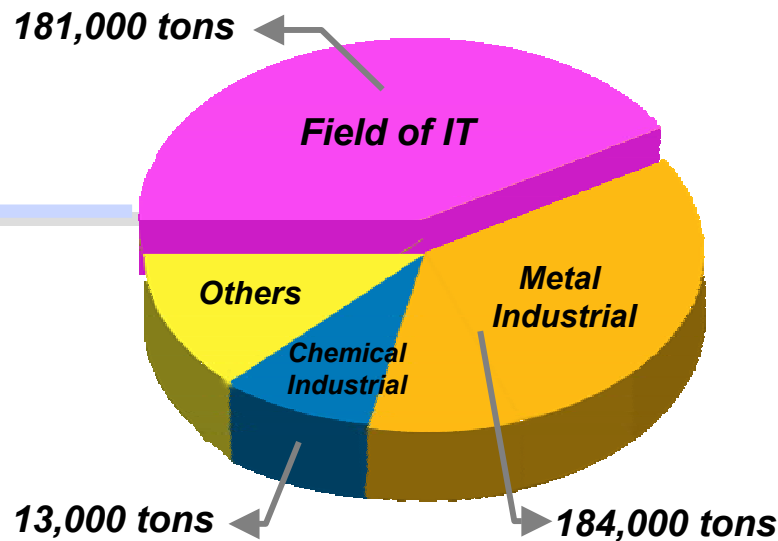
Research Institute of Industrial Science & Technology

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Present State of Industrial Waste Acid



The state of the waste acid

742,000 tons/year
(in 2002 standard)



25.8% of total industrial waste discharged
(The source of resource recycling white book)

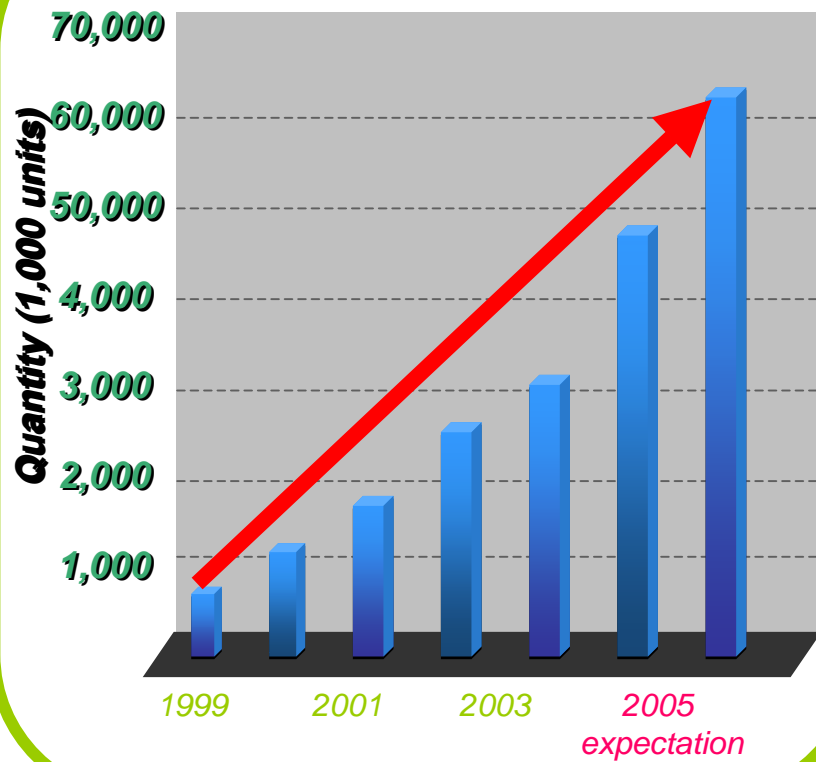
(Units: tons/year)

Waste acid	Semiconductor etchant	MLB etchant	MLB plating	MLCC manufacture	LCD etchant	PCB etchant	AI pickling	STS pickling
Discharge amount	22,000	4,800	3,500	4,500	60,000	30,000	80,000	7,000



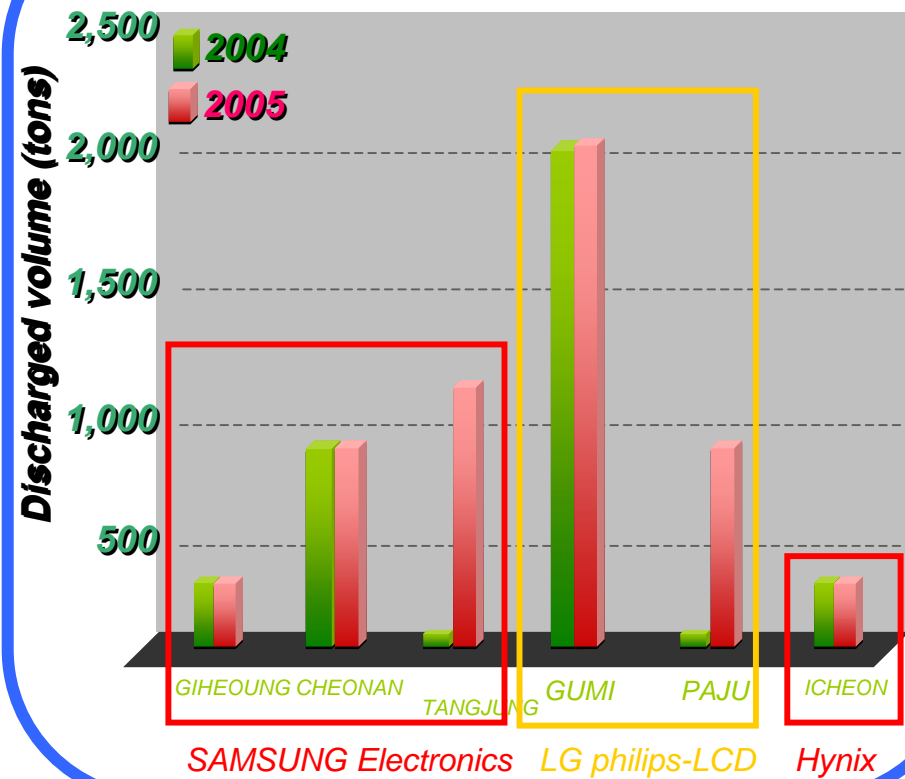
The Situation of LCD Manufacturing

Recent progress in production of LCD manufacturing



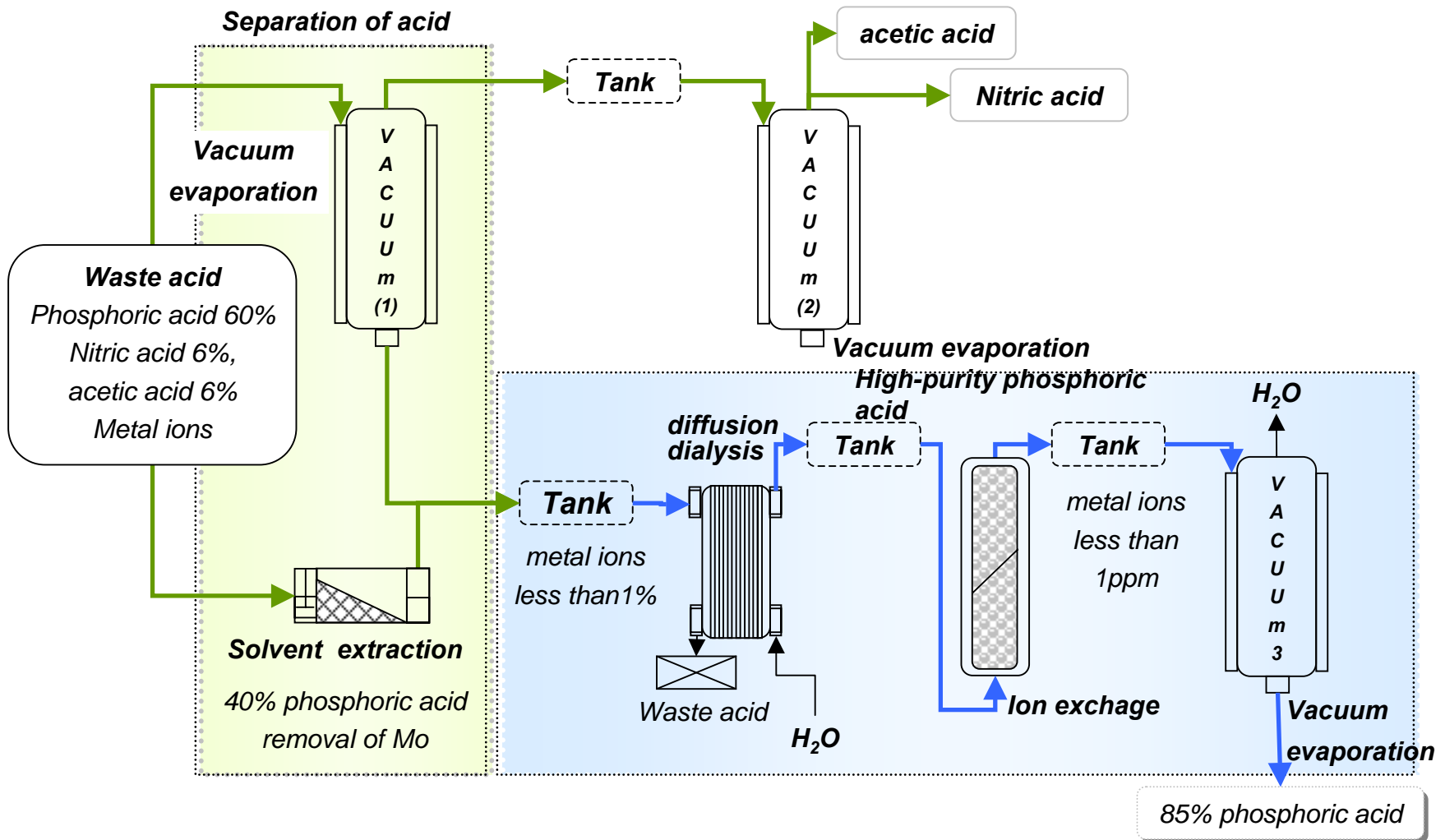
The source of Korea Electronics Technology Institute

Discharge industrial waste solution by manufacturers



Present discharged amount : above 5000 tons/month in 2005

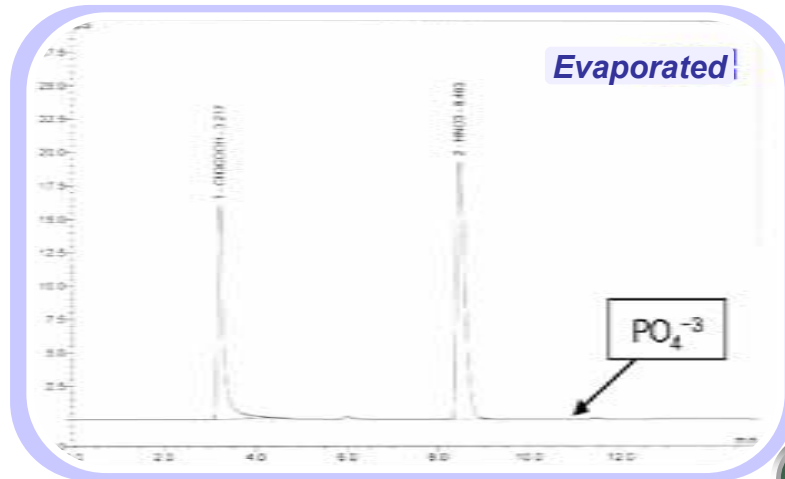
The Recovery of Phosphoric Acid



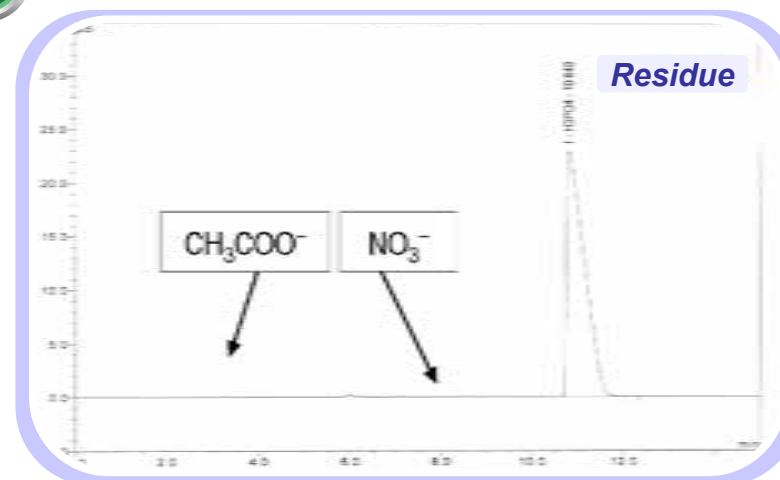
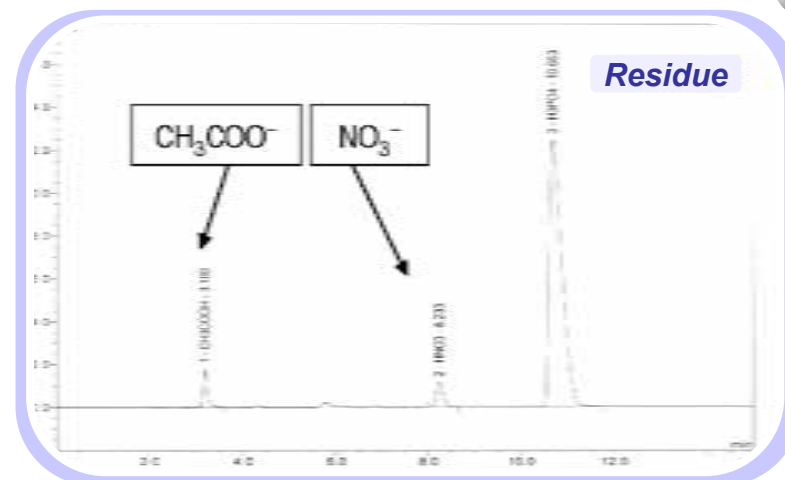
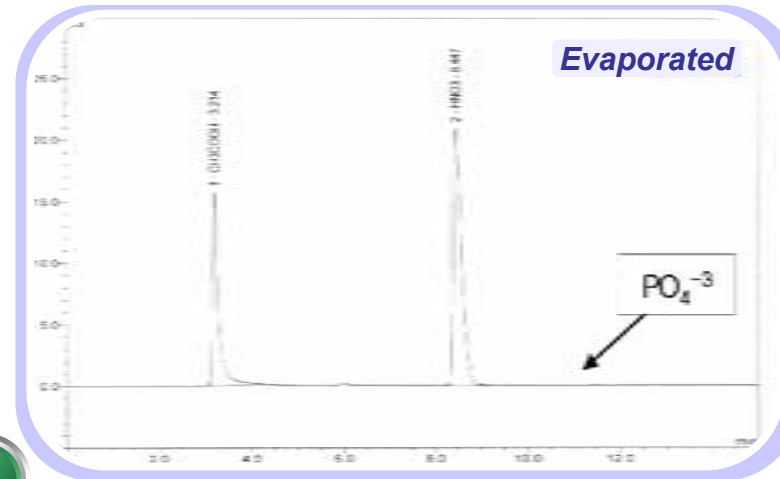


The Removal of Nitric Acid and Acetic acid by vacuum Evaporation

Degree of vacuum(-670mmHg), Temp.(120)



Degree of vacuum(-670mmHg), Temp.(140)



Separation of nitric acid and acetic acid by controlling the degree of vacuum and temperature

The recovery of phosphoric Acid From the Waste Acid in LCD Manufacturing

Test range : under degree of vacuum -670~760mmHg, 100~160 at temperature

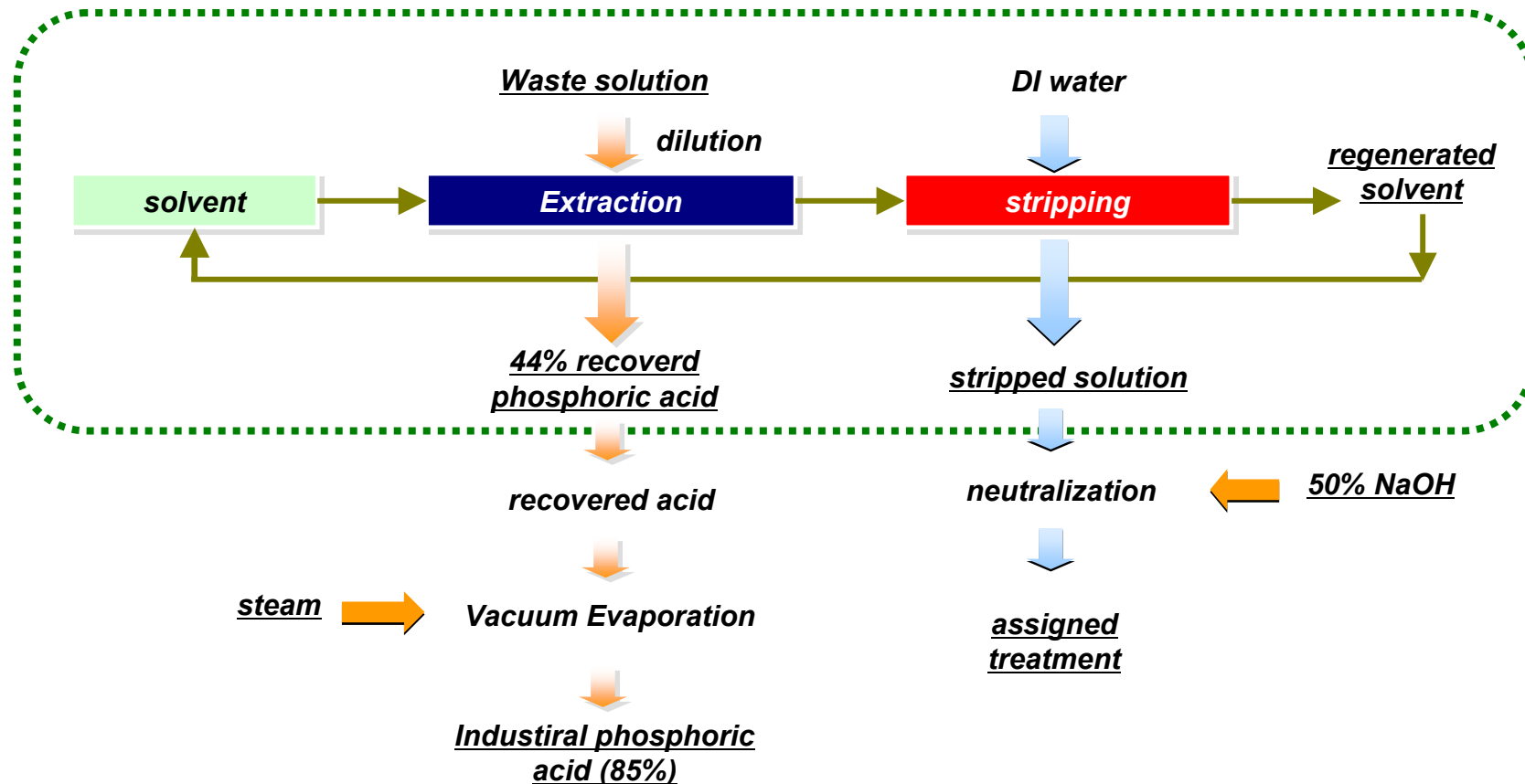
Commercial range : under degree of vacuum -750mmHg, 130 at temperature

Degree of vacuum	Concentration of phosphoric acid					Remarks	
-700 mmHg	Comp. Temp.(°C)	Concentration (g/kg)			Recovery of acid(%)		
		CH ₃ COOH	HNO ₃	H ₃ PO ₄	CH ₃ COOH	HNO ₃	
	100	11.62	11.88	796.62	86	86.3	
	110	6.95	0	810.41	92	94.0	
125	0	0	807.33	95.3	97.4		
-730 mmHg	▪ Removal of nitric and acetic acid above 110 .						
	Comp. Temp.(°C)	Concentration (g/kg)			Recovery of acid(%)		
		CH ₃ COOH	HNO ₃	H ₃ PO ₄	CH ₃ COOH	HNO ₃	
	100	8.66	0	790.09	95.3	95.3	
110	0	0	824.88	100	100		
125	0	0	841.84	100	100		

The Process of Solvent Extraction For the Removal of nitric acid and acetic acid

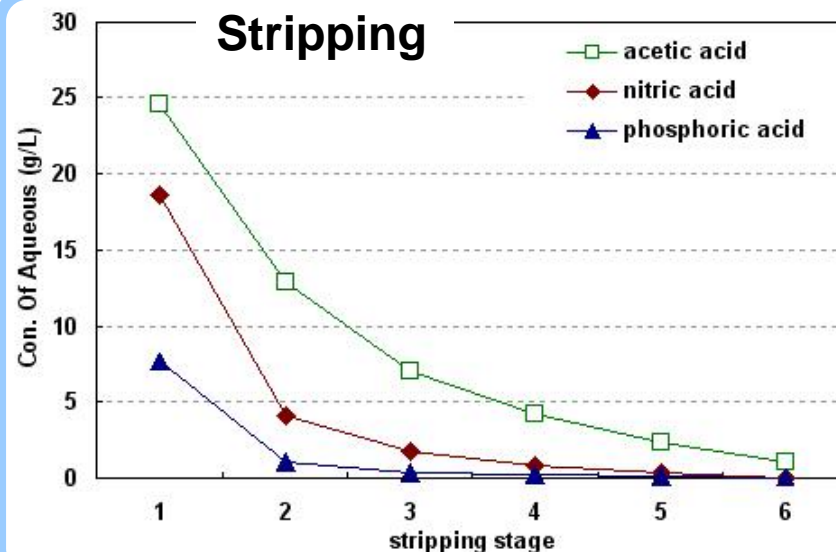
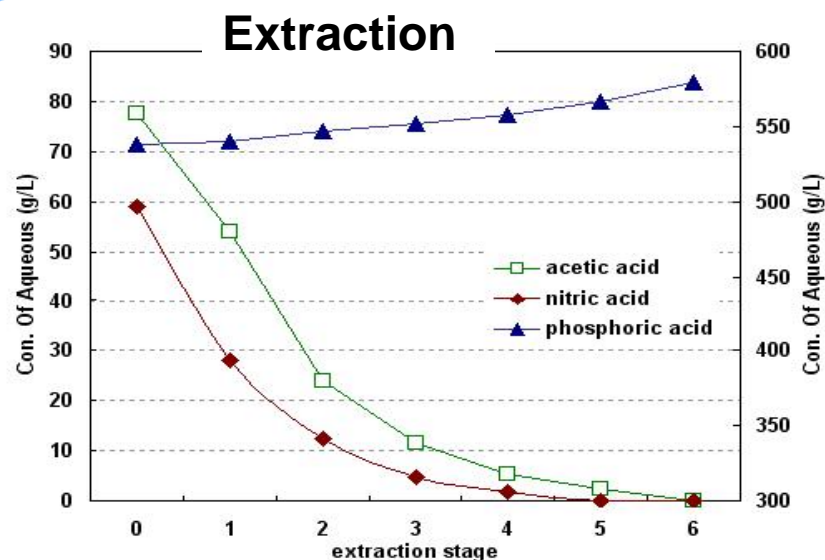
The composition of 40wt% diluted phosphoric acid

composition	acetic acid	nitric acid	phosphoric acid
concentration (g/L)	77.5	58.9	537.7





The Result of Bench Scale Testing



Test Condition

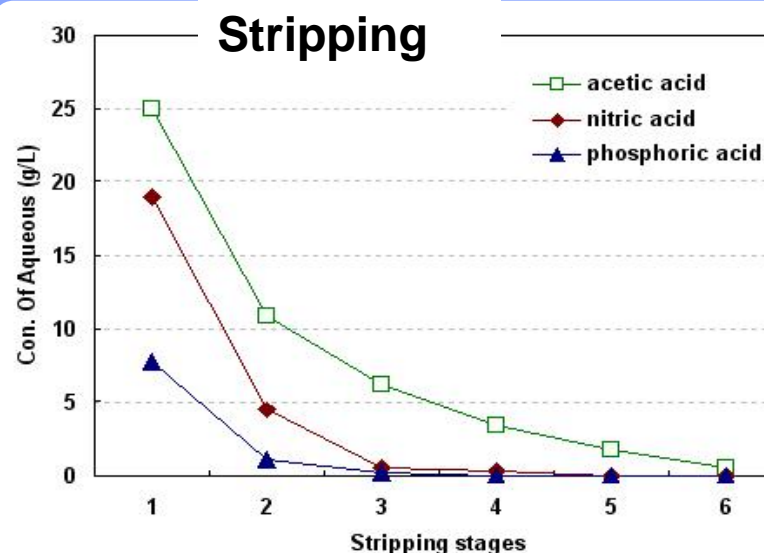
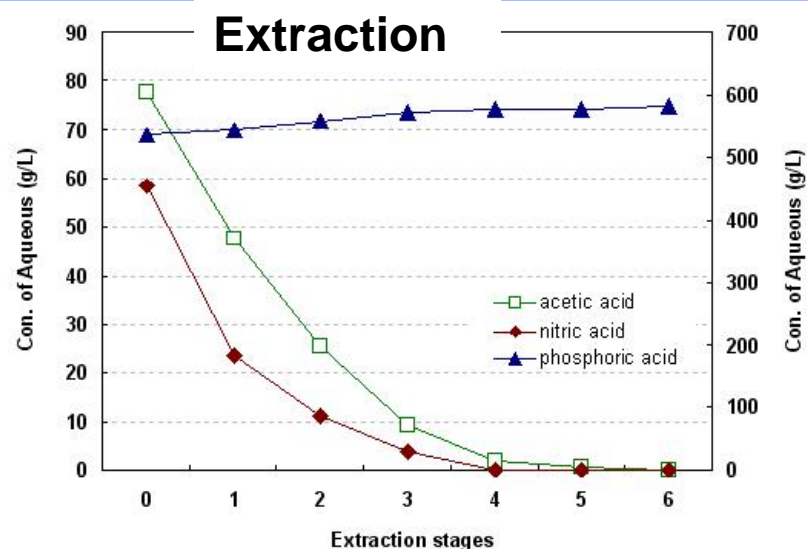
1. Stages : 6 stage extraction, 6 stages stripping
2. Concentration : diluted waste acid
(H_3PO_4 : 40wt%)
3. A/O ratio: 1/3
4. Conc. of Solvent: 50vol%(TOP/kerosine)

Result

1. Extraction stages
 - Removal of nitric acid : 5 stages
 - Removal of acetic acid : 6 stages
2. Recovery of H_3PO_4 : above 95%
3. Regenerated Solvent : 6 stage stripping
(uniform concentration of recovered acid)



The Result of Pilot Scale Testing



Test Condition

1. Stages : 6 stage extraction, 6 stages stripping
2. Concentration : diluted waste acid
(H_3PO_4 : 40wt%)
3. A/O ratio : 1/3
4. Conc. of Solvent: 50vol%(TOP/kerosine)

Result

1. The extraction of nitric acid and acetic acid is more effective in Pilot scale testing
2. The recovery of H_3PO_4 and regeneration of solvent is similar to the result of Bench scale testing.

The removal of metal ions by diffusion dialysis

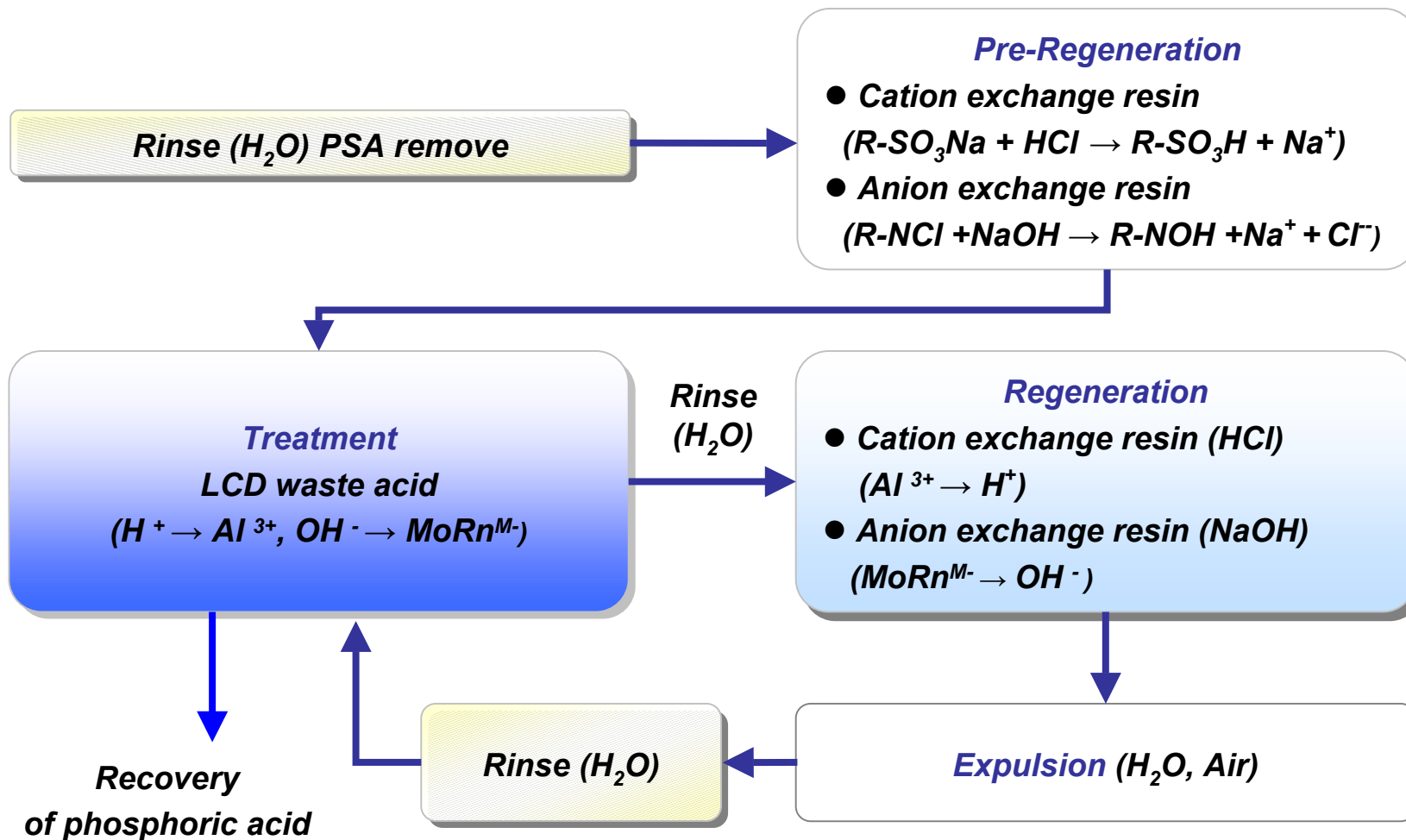


Component	Waste acid	Recovered acid	Dialysate	Removal of metal ions (%)	Remarks
H_3PO_4 (g/kg)	226.34	87.78	156.95	-	Recovery of H_3PO_4 38.78%
Al (mg/kg)	74.99	1.93	87.3	97.35	
Mo (mg/kg)	70.64	26.20	17.62	75.06	



*Preliminary runs of ion exchange process
Reduction of the capacity for ion exchange,
adjusting concentration of phosphoric acid, 21%
Removal of impurities (%) : Al 97.3%, Mo 75.0%*

The removal of metal ions by ion exchange

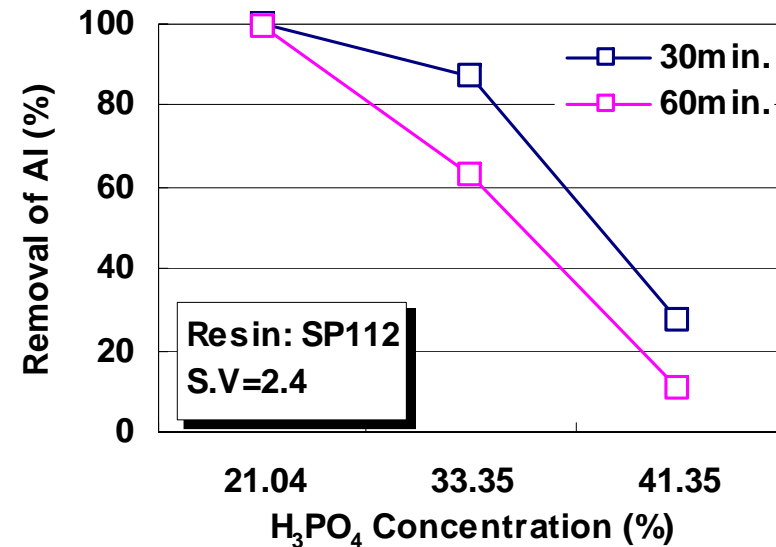
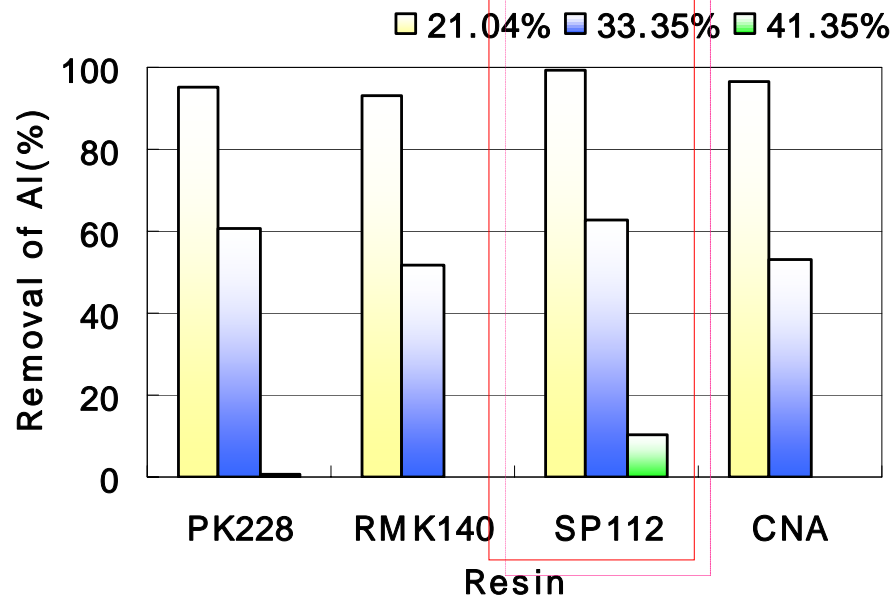




The removal of Al with cation exchange resin

Test Conditions

- Crude phosphoric acid :
RIST manufacture H_3PO_4 (Al contains)
- H_3PO_4 Concentration : 21.04%, 33.35%, 41.35%
- Column: 35mmx 200mm (glass)
- Resin volume: 100mL

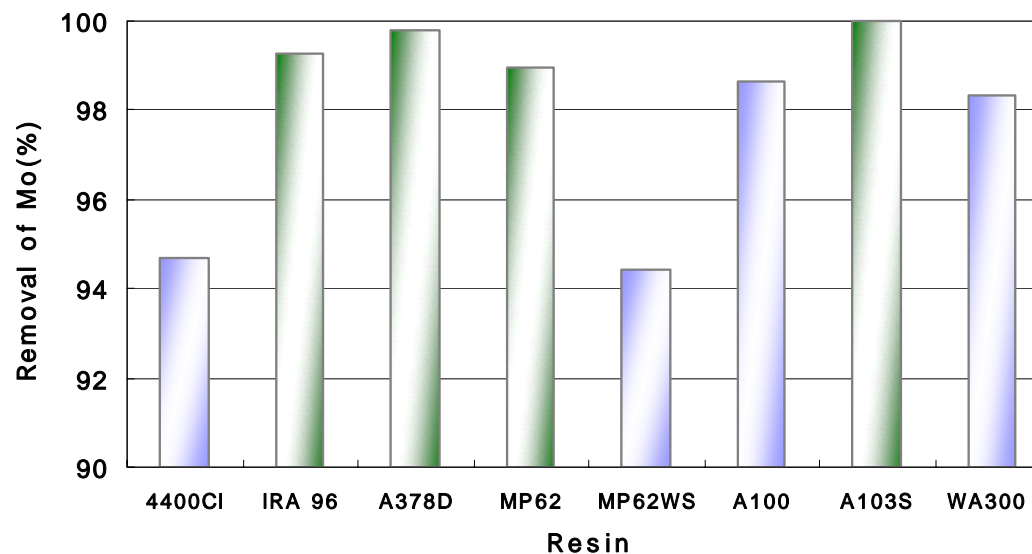


- Removal of Al with cation exchange resin
- Removal of Al is effective as concentration of H_3PO_4 decreases
- Monoplus SP112(Bayer Chemicals) Na type (porous type) is the most efficient
- 21.04% H_3PO_4 99.4% removal of Al

The removal of Mo with anion exchange resin

Test conditions

- Crude phosphoric acid :
RIST manufacture 22.52% H_3PO_4
(Mo contains)
- Initial Conc. of Mo: 72.56 mg/kg
- Column : 24mmx220mm
- Regeneration : 10%NaOH, S.V =4.0
- Rinse: S.V =10.0 (BV=20)
- Service : S.V =2.5 (60min)



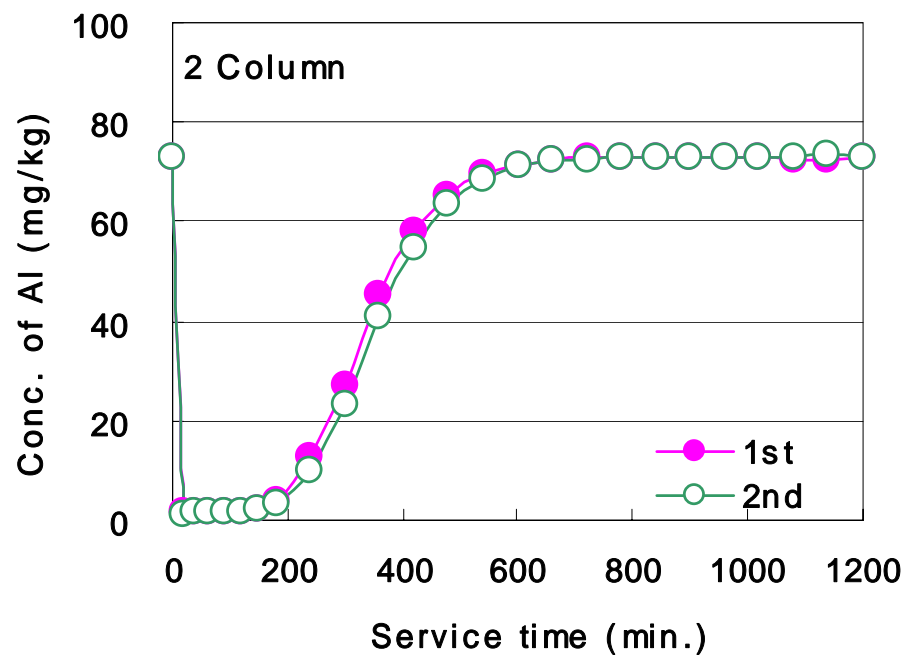
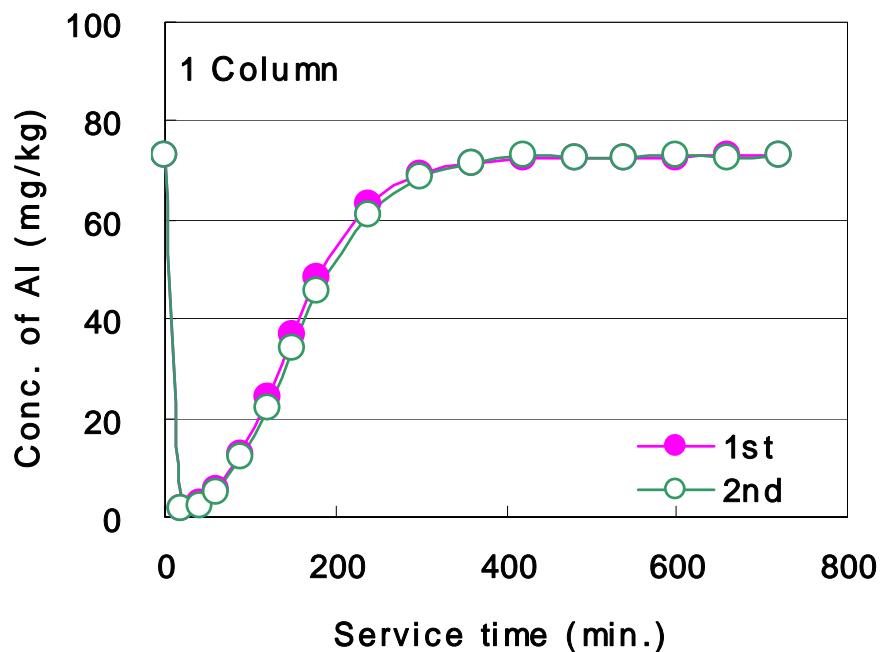
Component Resin	Mo (mg/kg)	Removal of Mo (%)	Component Resin	Mo (mg/kg)	Removal of Mo (%)
4400CI	3.86	94.7	MP62WS	4.05	94.4
IRA 96	0.54	99.3	A100	0.99	98.6
A378D	0.16	99.8	A103S	0.00	100
MP62	0.74	99.0	WA300	1.23	98.3

- Weakly basic anion exchange resin



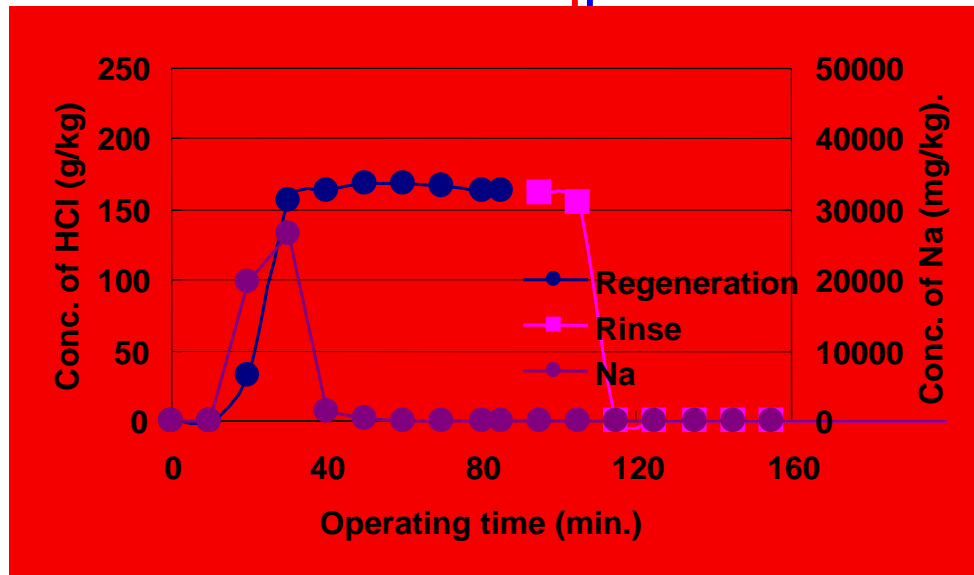
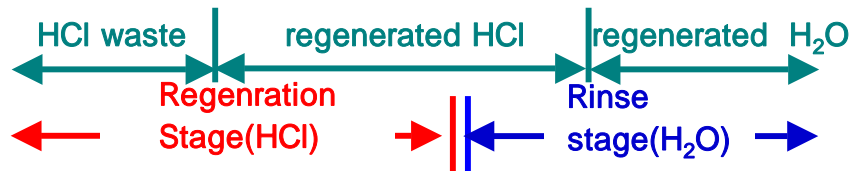
Evaluation of regeneration efficiency

● **Regeneration: 15% HCl, S.V=4.0, B.V=2**



➤ **regeneration efficiency of resin is efficient with regeneration solution of 15% HCl**

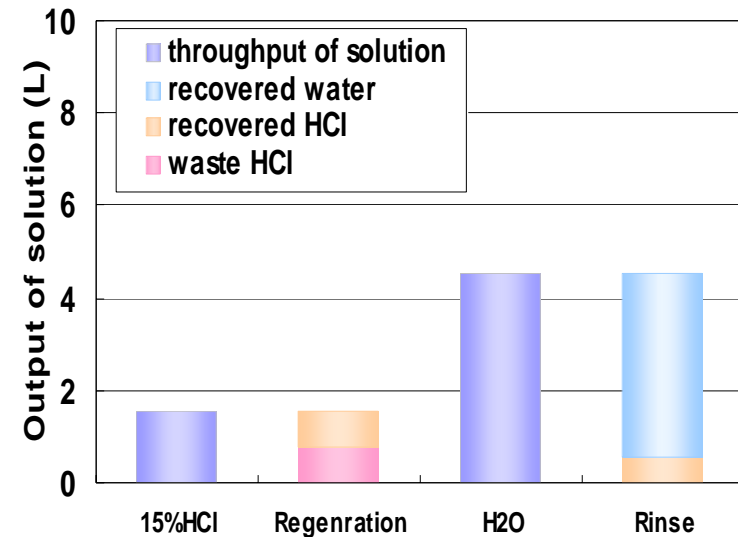
Evaluation of regenerate wastewater



Test conditions

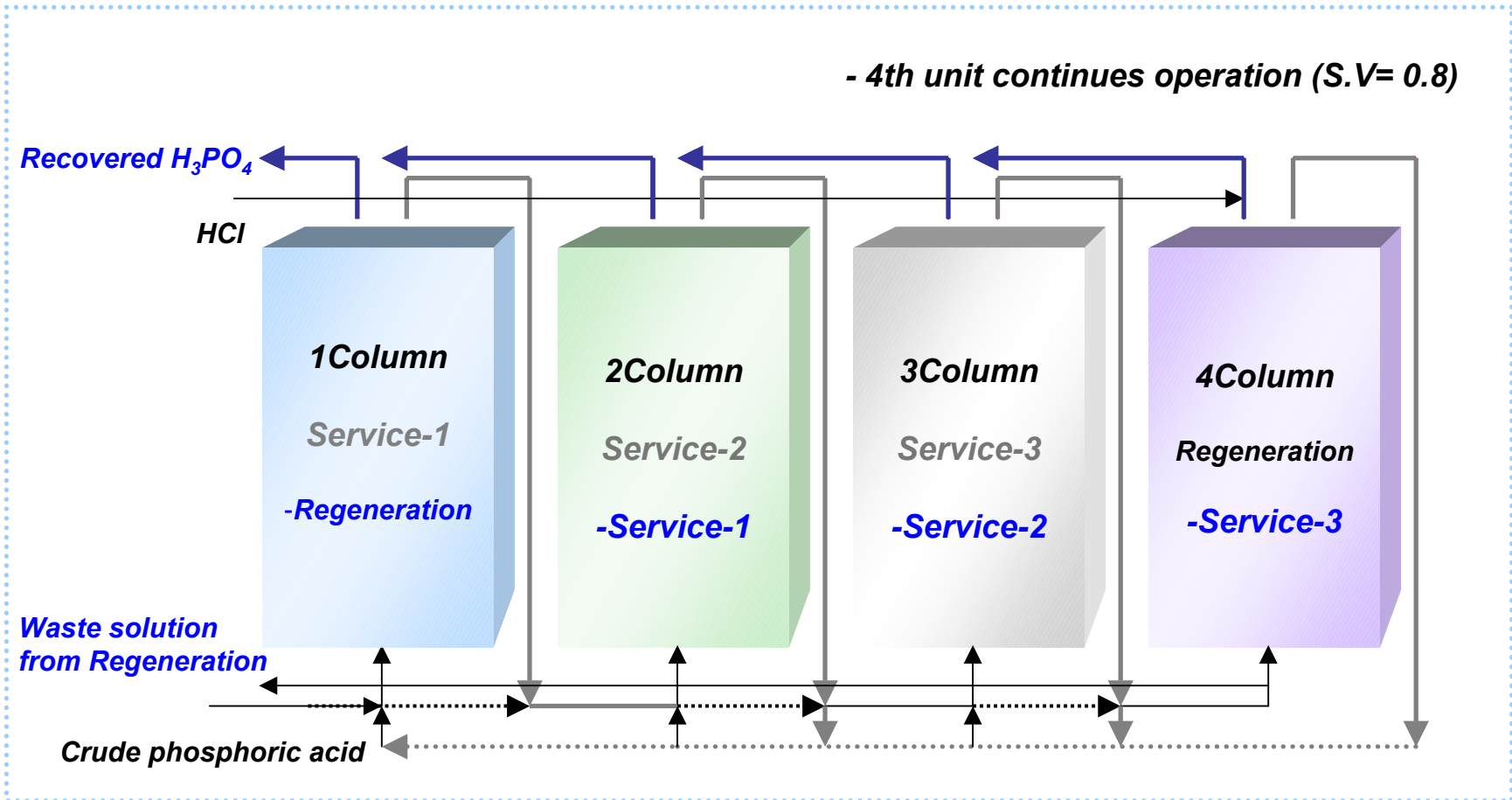
- **Regeneration:**
15% HCl (S.V=4.0)
- **Rinse:** water (S.V=10.0)

- *The discharged HCl and H₂O after regeneration and rinse is reusable*
- *about 88% recovery of HCl for regeneration solution*
- *about 87.6% recovery of H₂O for rinse solution*





The process of continues operation





Summary

✓ **The establishment of conditions for the removal of nitric acid and acetic acid from the mixed waste acid by vacuum evaporation**

: degree of vacuum, temperature (-700mmHg, 120)

✓ **The establishment of conditions for the removal of nitric acid and acetic acid by solvent extraction**

: phase ratio A/O= 1/3, nitric acid 5 stages, acetic acid 6 stages

✓ **The removal of metal ions (impurities) by diffusion dialysis**

: 97.3% removal of Al, 75.0% removal of Mo, organic phase; TOP

✓ **The removal of metal ions by ion exchange technology**

Al: SP112 (strong cation exchange resin), 99.4% removal, 21.04% H_3PO_4

Mo; A103S (weakly anion exchange resin, 100% removal, 22.5% H_3PO_4

✓ **The establishment of continuous process of recovering phosphoric acid for efficient automation of system**