Using Process Simulation to Predict Wastewater Treatment Outcomes

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Abstract

Changes occur rapidly in the semiconductor industry. New tools, new processes and the need to increase process capacity greatly impact downstream activities, notably wastewater treatment. The ability to predict how process changes affect water treatment will help to drive better wastewater handling methods, as critical areas of concern are identified *aprioi*. This paper examines the outcome of four waste treatment applications designed on the computer using real-solution aqueous process simulation.

First, two typical fluoride waste water streams were treated with either $Ca(OH)_2$ or $CaCl_2$. Process simulation was used to predict the chemical addition rate, and the clean water composition following CaF_2 removal. The predictions favorably compared to results achieved in the lab on synthetic wastewater samples; differences were attributed to limitations in the lab experimental procedures. Next, the effect of neutralization on dilute acid waste composition was explored by process simulation. It was shown that subtle changes can cause huge swings in species concentrations of wastewater. Third, the alumina and silica solubility in CMP waste was predicted, and it was pointed out how the data could be used to design a full-scale system.

Lastly, it was determined how pH and ligand concentrations affected copper solubility in Cu CMP wastewater. Simulation predicted that 1,000 ppm of ammonia in the waste would cause the treated water to exceed discharge limitation unless a very high pH set point was used. The process simulation software was used to support the development and design of a process to treat Cu CMP wastewater, which was successfully piloted and commercialized.

Introduction

Due to rapid technological advances, production processes in the semiconductor industry quickly change. For instance, according to the *1998 Update to the International Technology Roadmap for Semiconductors*,[1] design cycle times in 1999 should decrease by 20% over 1997 design cycle times; cycle times in 2002 will decrease by 35% over 1997 cycle times. Dense line width will decrease from 250 nm in 1997 to 130 nm in 2002. For construction of new factories, the roadmap goal is to reduce the time to first wafer start from 23 months in 1997 to 16 months in 2002. The production ramp time to maximum capacity is to be shortened from 9 months in 1997 to 5 months in 2002. The time to the mature yield level is to be cut from 4 years in 1997 to 1.5 years in 2002. High performance chip frequency is to be increased from 750 MHz in 1997 to 2100 MHz in 2002.

In order to meet these and other goals, new processes and chemistries will be introduced. Existing infrastructure, such as downstream wastewater treatment, must accommodate these newly introduced processes and chemistries, or new infrastructure must be built. The cycle time for accommodation or construction of infrastructure must match the cycle time for introduction of new technologies. Tools for decreasing the wastewater treatment process development cycle time would be welcome additions to the arsenal of tools used by facilities managers at semiconductor fabs. Aqueous process simulation software is one such tool. The ability to model different scenarios for wastewater treatment before actually producing the wastewater can shorten development times. Process simulation software can facilitate preliminary system design, and pinpoint critical areas of study in laboratory work, piloting and scale-up. When

problems occur in the full-scale system, the software could be used to model problem sources and potential solutions.

Process Simulation Software

Process simulation software has seen extensive use in the refining, petrochemical, and allied chemical industries, with well-known packages available from AspenTech[2] and Simulation Sciences, Inc.[3] The entire paper making process, from pulp wood to wastewater, has been modeled using process simulation software called WinGEMS from Pacific Simulations, Inc.[4] The Environmental Protection Agency and others use process simulation software for industrial pollution prevention.[5] Aqueous process simulation software includes Environmental Simulation Program (ESP) and other programs from OLI Systems[6], and several software programs offered by French Creek Software.[7]

Process simulation involving electrolytes in an aqueous environment is very complex due to the many sets of equilibria that are possible in a multi-component system. The aqueous electrolyte engine developed by OLI Systems is also licensed and used in the AspenTech and Simulation Sciences, Inc. process simulation software for instances where aqueous solutions of strong electrolytes are modeled. After evaluating the available software, it was decided to focus on ESP and associated programs from OLI Systems.

The OLI engine uses a "thermodynamic and mathematical framework for predicting the equilibrium properties of a chemical system" details of which[8] are beyond the scope of the present publication. It is important to remember that, unless kinetics are explicitly taken into account, the results obtained from ESP are based only on thermodynamics.

Hydrofluoric Acid Wastewater Treatment with Lime

A common class of semiconductor wastewater is hydrofluoric acid (HF) wastes produced from wafer etch operations. Typical concentrations of HF are from 100 to 1,000 ppm, although

concentrations as high as 10,000 ppm have been seen. Publicly owned treatment works (POTW) limit fluoride discharge levels to less than 20 ppm, with some localities below 15 ppm fluoride. Well-known methods for meeting the discharge limitation include addition of either lime ($Ca(OH)_2$) or calcium chloride ($CaCl_2$) to the wastewater to precipitate calcium fluoride (CaF_2), which is removed by clarification or filtration. The stoichiometry of the reaction with lime is shown in equation 1 below. Note that lime acts as both a calcium source and as a base to neutralize the protons. The CaF_2 precipitates from the reaction mixture, driving the equilibrium to the right, favoring the removal of the fluoride down to the solubility limit of CaF_2. For every mole of HF, 0.5 mole of $Ca(OH)_2$ is used.

$$2HF + Ca(OH)_2 \rightleftharpoons CaF_2 \text{ (ppt)} + 2H_2O \quad (1)$$
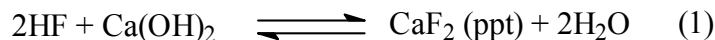
The reaction with $CaCl_2$ is more complex, as shown by equations 2 and 3, and the summary equation 4.

$$2HF + CaCl_2 \rightleftharpoons CaF_2 \text{ (ppt)} + 2 HCl \quad (2)$$

$$2HCl + 2NaOH \rightleftharpoons 2NaCl + 2H_2O \quad (3)$$

$$\overline{2HF + CaCl_2 + 2NaOH \rightleftharpoons CaF_2 \text{ (ppt)} + 2NaCl + 2H_2O \quad (4)}$$

The reaction of $CaCl_2$ with HF produces CaF_2, which precipitates, and HCl. At the low pH of equation 2, the equilibrium lies farther to the left than in equation 1, and the concentration of fluoride in solution remains higher than 20 ppm. Neutralization of the HCl is necessary in order to drive the reaction to the right, and remove more of the soluble fluoride. Sodium hydroxide is typically used, as shown in equation 3. This produces NaCl as a by-product. The summary equation 4 shows that for every mole of HF, one mole of NaOH and 0.5 mole of $CaCl_2$ are needed.

While most HF wastewater streams are complex mixtures of acids and bases in addition to HF, process simulation of a simple waste containing only HF represents a first step in learning about the requirements and pit-falls of the software, and the results can be easily benchmarked against

experience. Earlier work has been published which utilized the **ChemSage** process simulation program[9].

Figure 1

lime flow controller

20% lime

HF Stream

Separator

pH meter

clean water

CaF2 solids
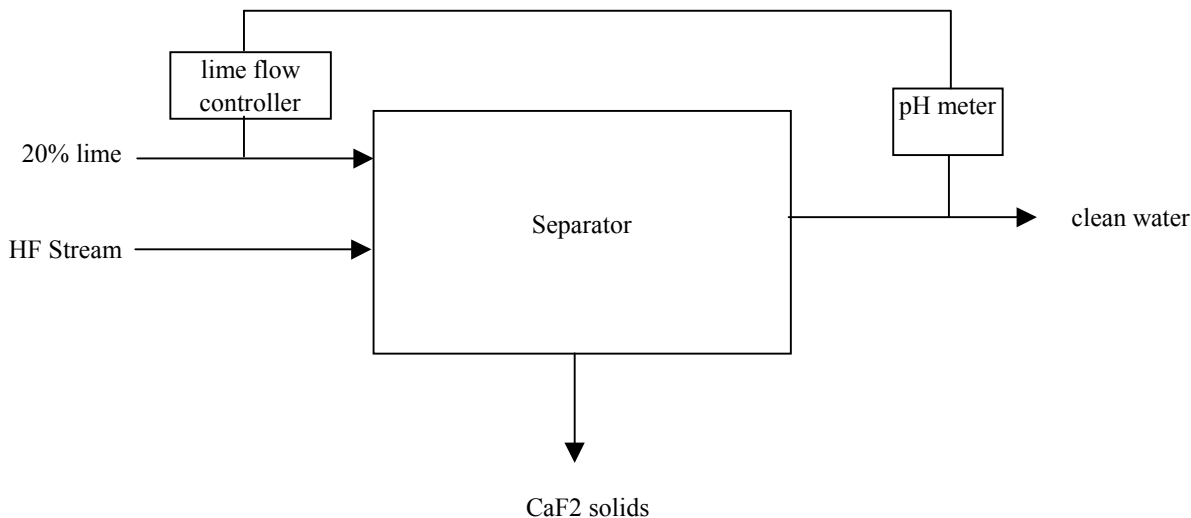
The treatment of HF wastewater can be easily modeled in **ESP** using a unit process called a "separator," which separates solids and gases from a liquid stream. The process flow diagram (PFD) used in the model is shown in Figure 1 above. Since no vapor was produced in the process, no vapor stream is depicted in the PFD. In Figure 1, the HF waste stream flowed into the separator at an arbitrary rate of 100 gpm, 25°C temperature, and 1 atmosphere (atm) pressure. In the separator, the HF stream reacted with a separately introduced 20% lime slurry stream (also at 25°C and 1 atm) to produce solid CaF_2. One could either use entrainment calculations or equilibrium calculations to determine the amount of solids produced. Adiabatic equilibrium calculations were used in this and all following studies. A pH meter was used to monitor the reaction of the lime with the HF. The pH information was used to drive a lime flow controller. The flow controller manipulated the flow of the lime until the pH set-point target of the clean water was achieved. This is the same control system used in commercial treatment systems.

In the example, an HF waste stream containing 1,000 ppm HF was treated with lime to a pH set point of 11. The tolerance of the model was set to ±0.1 pH units. One can choose different output units for **ESP** data. Weight fraction output units were used for the chemical components,

Table 1

Treatment of 1,000 ppm HF Waste With 20% Lime at pH = 11

Stream	HF	manipulated slurry		clean water	CaF2	HF	manipulated slurry		clean water	CaF2
Phase	Aqueous	Aqueous	Solid	Aqueous	Solid	Aqueous	Aqueous	Solid	Aqueous	Solid
Temperature, C	25.00	25.00	25.00	26.12	26.12	25.00	25.00	25.00	26.12	26.12
Pressure, atm	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
pH	2.28	12.39		11.05		2.28	12.39		11.05	
Total mol/min	20,971.70	159.62	9.65	21,130.00	9.40	20,971.70	159.62	9.65	21,130	9.40
Flow Units	**wtfrac**	**wtfrac**	**wtfrac**	**wtfrac**	**wtfrac**	**ppm**	**ppm**	**ppm**	**ppm**	**ppm**
H2O	9.99E-01	9.99E-01		1.00E+00		999,000	998,755		999,943	
H2F2	1.53E-09			6.59E-30		0.00			0.00	
HF	8.85E-04			5.76E-14		884.73			0.00	
OHION	3.56E-14	5.18E-04		2.23E-05		0.00	517.72		22.28	
FION	1.07E-04			3.98E-06		107.16			3.98	
HF2ION	2.37E-06			5.70E-18		2.37			0.00	
HION	5.75E-06	5.00E-16		9.44E-15		5.75	0.00		0.00	
CAION		5.47E-04		3.02E-05			546.62		30.17	
CAOHION		1.81E-04		7.86E-07			180.58		0.79	
CAOH2			1.00E+00					1,000,000		
CAFION				5.99E-10					0.00	
CAF2					1.00E+00					1,000,000
Total g/min	377,820	2,876.67	714.70	380,680	734.10	377,820	2,876.67	714.70	380,680	734.10
Volume, gal/min	100.00	0.76	0.08	100.91	0.06	100.00	0.76	0.08	100.91	0.06
Enthalpy, Btu/min	-5,681,600	-43,252	-9,014	-5,722,800	-11,011	-5,681,600	-43,252	-9,014	-5,722,800	-11,011
Density, g/gal	3,778	3,779	8,479	3,773	12,043	3,778	3,779	8,479	3,772.62	12,043
Osmotic Pres, atm	1.35E+00	1.01E+00		5.39E-02		1.35E+00	1.01E+00		5.39E-02	
E-Con, 1/ohm-cm	2.25E-03	6.33E-03		3.49E-04		2.25E-03	6.33E-03		3.49E-04	
E-Con, cm2/ohm-mol	4.52E+01	1.88E+00		4.85E+00		4.52E+01	1.88E+00		4.85E+00	
Abs Visc, cP	8.92E-01	9.00E-01		8.69E-01		8.92E-01	9.00E-01		8.69E-01	
Rel Visc	1.00E+00	1.01E+00		1.00E+00		1.00E+00	1.01E+00		1.00E+00	
Ionic Strength	5.71E-03	4.41E-02		2.27E-03		5.71E-03	4.41E-02		2.27E-03	

since weight fraction can be easily converted to ppm. The data is shown in Table 1, which is divided into weight fraction and ppm sections. The five process streams are shown in columns, repeated in the weight fraction and ppm sections. The HF waste stream is first, followed by the manipulated lime stream. Since the lime stream is in slurry form, **ESP** separates it into aqueous and solid streams. The fourth stream is the clean water, and the fifth stream is the solid CaF_2. Note that the solid CaF2 stream is 100% solid, while in actuality it would contain from 30 to 60% water by weight.

Temperature, pressure, pH, and mole flow data are shown across the top of Table 1; the composition of each stream is shown in the middle of Table 1, while stream flows and other data are shown in the bottom third of Table 1. In examining the data one needs to remember that the results are based on thermodynamic calculations, not the kinetics of the reactions. The flow rate only dictates the mass of material treated per unit time. Since one is not concerned with kinetics, reactor size and retention times do not enter in to the calculations.

Referring to the data in Table 1, the heat of reaction drove the temperature of the clean water up to 26.12°C. The total flow of the clean water was 100.91 gpm. The pH of the HF waste was 1.73; the pH of the aqueous 20% lime was 12.39; and the pH of the clean water was 11.05. It took 0.84 gpm of 20% lime slurry to hit the target pH. All of this information can be useful in developing preliminary equipment designs, sizes, and materials of construction.

The clean water was predicted to contain 3.98 ppm of fluoride ion, which easily met discharge limitations. **ESP** also estimated that the clean water contained 5.76×10^{-14} wt fraction of HF; this became vanishingly small on conversion to ppm. While this may seem to be extraneous information for the present study, the ability to predict the composition of water contaminants to such low levels could lead to better methods of detection and analysis. Additionally, as the industry drives toward higher purity specifications for chemicals and water, prediction of ionic components at very low levels may lead to better purification methods.

Treatment of a fluoride wastewater stream containing 10,000 ppm HF was also modeled, with the same pH target of 11 using 20% lime. The results from model are given in Table 2. Since

Table 2

Treatment of 10,000 ppm HF Waste With 20% Lime at pH = 11

Stream	HF	manipulated slurry		clean water	CaF2	HF	manipulated slurry		clean water	CaF2
Phase	Aqueous	Aqueous	Solid	Aqueous	Solid	Aqueous	Aqueous	Solid	Aqueous	Solid
Temperature, C	25.00	25.00	25.00	35.59	35.59	25.00	25.00	25.00	35.59	35.59
Pressure, atm	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
pH	1.73	12.39		11.03		1.73	12.39		11.03	
Total mol/min	21,195.00	1,580.82	95.53	22,768.30	95.45	21,195.00	1,580.82	95.53	22,768.30	95.45
Flow Units	**wtfrac**	**wtfrac**	**wtfrac**	**wtfrac**	**wtfrac**	**ppm**	**ppm**	**ppm**	**ppm**	**ppm**
H2O	9.90E-01	9.99E-01		1.00E+00		990,000	998,755		999,898	
H2F2	1.87E-07			8.29E-30		0.19			0.00	
HF	9.53E-03			5.85E-14		9,532.13			0.00	
OHION	1.07E-14	5.18E-04		4.25E-05		0.00	517.72		42.46	
FION	3.59E-04			3.57E-06		358.67			3.57	
HF2ION	8.77E-05			5.29E-18		87.73			0.00	
HION	2.13E-05	5.00E-16		1.00E-14		21.30	0.00		0.00	
CAION		5.47E-04		5.28E-05			546.62		52.80	
CAOHION		1.81E-04		2.84E-06			180.58		2.84	
CAOH2			1.00E+00					1,000,000		
CAFION				1.63E-09					0.00	
CAF2					1.00E+00					1,000,000
Total g/min	382,080	28,490	7,078.17	410,180	7,452.17	382,080	28,490	7,078.17	410,180	7,452.17
Volume, gal/min	100.00	7.54	0.83	109.05	0.62	100.00	7.54	0.83	109.05	0.62
Enthalpy, Btu/min	-5,745,300	-428,350	-89,268	-6,151,200	-111,720	-5,745,300	-428,350	-89,268	-6,151,200	-111,720
Density, g/gal	3,821	3,779	8,479	3,762	12,043	3,821	3,779	8,479	3,762	12,043
Osmotic Pres, atm	1.30E+01	1.01E+00		9.71E-02		1.30E+01	1.01E+00		9.71E-02	
E-Con, 1/ohm-cm	8.35E-03	6.33E-03		7.32E-04		8.35E-03	6.33E-03		7.32E-04	
E-Con, cm2/ohm-mol	1.66E+01	1.88E+00		1.07E+00		1.66E+01	1.88E+00		1.07E+00	
Abs Visc, cP	8.95E-01	9.00E-01		7.12E-01		8.95E-01	9.00E-01		7.12E-01	
Rel Visc	1.00E+00	1.01E+00		1.00E+00		1.00E+00	1.01E+00		1.00E+00	
Ionic Strength	2.13E-02	4.41E-02		4.00E-03		2.13E-02	4.41E-02		4.00E-03	

more fluoride was present, the heat of reaction increased the temperature of the clean water to 35.59°C. The volume of clean water was 109.05 gpm, the result of adding 8.37 gpm of 20% lime slurry to bring the pH of the clean water to 11.05.

What if the target pH was 8 instead of 11? How does this affect temperature, volume, chemical usage, and fluoride content? Treatment of both the 1,000 ppm and 10,000 ppm HF streams at pH 8 using the process of Figure 1 were modeled using **ESP**; the results are shown in Tables 3 and 4, respectively. Since the pH curve at 8 is quite steep, and it's difficult to hit a specific target with the high concentration of the 20% lime slurry, the pH tolerance had to be set at ±0.5 pH units in order to get the calculations to converge.

At the lower pH, the fluoride ion content of the water rose to 7.3-7.9 ppm from the 3.5-4.0 ppm values at the higher pH of 11. There was a very slight decrease in lime usage at the lower pH, about 0.02 to 0.04 gpm less than at pH 11. This led to a slight decrease in the volume of the clean water stream.

In a real-world application of process simulation software, a pilot system was operating on an HF wastewater stream using lime as the chemical reactant. The pilot was easily achieving the target discharge concentration of fluoride, below 20 ppm, when a sudden spike in the concentration of fluoride in the clean water occurred. It was postulated that an increase in ammonia concentration caused the problem, but samples were being analyzed off-site and results would not be returned for days. In a matter of hours, **ESP** predicted that a high ammonia concentration in the wastewater could have caused the fluoride spike. A solution to the problem was also modeled, and shown to work by subsequent pilot operation. The analytical results confirmed the presence of high levels of ammonia in the wastewater, at the same levels predicted by **ESP** to have caused the problem. The process modeling shaved days off the process development time.

Laboratory Confirmation of Fluoride Waste Lime Treatment

The modeling results were compared to the results of laboratory experiments designed to measure the soluble fluoride remaining after lime treatment of a synthetic fluoride waste. The

Table 3

Treatment of 1,000 ppm HF Waste With 20% Lime at pH = 8

Stream	HF	manipulated slurry		clean water	CaF2	HF	manipulated slurry		clean water	CaF2
Phase	Aqueous	Aqueous	Solid	Aqueous	Solid	Aqueous	Aqueous	Solid	Aqueous	Solid
Temperature, C	25.00	25.00	25.00	26.11	26.11	25.00	25.00	25.00	26.11	26.11
Pressure, atm	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
pH	2.28	12.39		8.43		2.28	12.39		8.43	
Total mol/min	20,971.70	155.48	9.40	21,125.00	9.37	20,971.70	155.48	9.40	21,125.00	9.37
Flow Units	wtfrac	wtfrac	wtfrac	wtfrac	wtfrac	ppm	ppm	ppm	ppm	ppm
H2O	9.99E-01	9.99E-01		1.00E+00		999,000	998,755		999,985	
H2F2	1.53E-09			4.00E-24		0.00			0.00	
HF	8.85E-04			4.49E-11		884.73			0.00	
OHION	3.56E-14	5.18E-04		5.23E-08		0.00	517.72		0.05	
FION	1.07E-04			7.27E-06		107.16			7.27	
HF2ION	2.37E-06			8.12E-15		2.37			0.00	
HION	5.75E-06	5.00E-16		3.82E-12		5.75	0.00		0.00	
CAION		5.47E-04		7.73E-06			546.62		7.73	
CAOHION		1.81E-04		5.24E-10			180.58		0.00	
CAOH2			1.00E+00					1,000,000		
CAFION				3.11E-10					0.00	
CAF2					1.00E+00					1,000,000
Total g/min	377,820	2,802.17	696.17	380,580	731.53	377,820	2,802.17	696.17	380,580	731.53
Volume, gal/min	100.00	0.74	0.08	100.89	0.06	100.00	0.74	0.08	100.89	0.06
Enthalpy, Btu/min	-5,681,600	-42,130	-8,780	-5,721,500	-10,973	-5,681,600	-42,130	-8,780	-5,721,500	-10,973
Density, g/gal	3,778	3,779	8,479	3,772	12,043	3,778	3,779	8,479	3,772	12,043
Osmotic Pres, atm	1.35E+00	1.01E+00		1.39E-02		1.35E+00	1.01E+00		1.39E-02	
E-Con, 1/ohm-cm	2.25E-03	6.33E-03		4.45E-05		2.25E-03	6.33E-03		4.45E-05	
E-Con, cm2/ohm-mol	4.52E+01	1.88E+00		6.24E-01		4.52E+01	1.88E+00		6.24E-01	
Abs Visc, cP	8.92E-01	9.00E-01		8.69E-01		8.92E-01	9.00E-01		8.69E-01	
Rel Visc	1.00E+00	1.01E+00		1.00E+00		1.00E+00	1.01E+00		1.00E+00	
Ionic Strength	5.71E-03	4.41E-02		5.79E-04		5.71E-03	4.41E-02		5.79E-04	

Table 4

Treatment of 10,000 ppm HF Waste With 20% Lime at pH = 8

Stream	HF	manipulated slurry		clean water	CaF2	HF	manipulated slurry		clean water	CaF2
Phase	Aqueous	Aqueous	Solid	Aqueous	Solid	Aqueous	Aqueous	Solid	Aqueous	Solid
Temperature, C	25.00	25.00	25.00	35.59	35.59	25.00	25.00	25.00	35.59	35.59
Pressure, atm	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
pH	1.73	12.39		8.48		1.73	12.39		8.48	
Total mol/min	21,195.00	1,572.24	95.01	22,758.30	95.40	21,195.00	1,572.24	95.01	22,758.30	95.40
Flow Units	wtfrac	wtfrac	wtfrac	wtfrac	wtfrac	ppm	ppm	ppm	ppm	ppm
H2O	9.90E-01	9.99E-01		1.00E+00		990,000	998,755		999,984	
H2F2	1.87E-07			5.49E-24		0.19			0.00	
HF	9.53E-03			4.76E-11		9,532.13			0.00	
OHION	1.07E-14	5.18E-04		1.15E-07		0.00	517.72		0.12	
FION	3.59E-04			7.88E-06		358.67			7.88	
HF2ION	8.77E-05			9.51E-15		87.73			0.00	
HION	2.13E-05	5.00E-16		3.41E-12		21.30	0.00		0.00	
CAION		5.47E-04		8.45E-06			546.62		8.45	
CAOHION		1.81E-04		1.45E-09			180.58		0.00	
CAOH2			1.00E+00					1,000,000		
CAFION				6.79E-10					0.00	
CAF2					1.00E+00					1,000,000
Total g/min	382,080	28,335	7,039.83	410,000	7,448.50	382,080	28,335	7,039.83	410,000	7,448.50
Volume, gal/min	100.00	7.50	0.83	109.01	0.62	100.00	7.50	0.83	109.01	0.62
Enthalpy, Btu/min	-5,745,300	-426,020	-88,786	-6,148,500	-111,670	-5,745,300	-426,020	-88,786	-6,148,500	-111,670
Density, g/gal	3,821	3,779	8,479	3,761	12,043	3,821	3,779	8,479	3,761	12,043
Osmotic Pres, atm	1.30E+01	1.01E+00		1.56E-02		1.30E+01	1.01E+00		1.56E-02	
E-Con, 1/ohm-cm	8.35E-03	6.33E-03		5.93E-05		8.35E-03	6.33E-03		5.93E-05	
E-Con, cm2/ohm-mol	1.66E+01	1.88E+00		8.68E-02		1.66E+01	1.88E+00		8.68E-02	
Abs Visc, cP	8.95E-01	9.00E-01		7.12E-01		8.95E-01	9.00E-01		7.12E-01	
Rel Visc	1.00E+00	1.01E+00		1.00E+00		1.00E+00	1.01E+00		1.00E+00	
Ionic Strength	2.13E-02	4.41E-02		6.33E-04		2.13E-02	4.41E-02		6.33E-04	

laboratory feed waste, containing either 1,000 ppm or 10,000 ppm HF, was synthesized with DI water as the base stock. Using a typical jar testing apparatus, a 1 L beaker of the waste was agitated with a paddle stirrer at a constant rate while solid lime was carefully added in small portions to achieve the target pH. The results of the laboratory tests are shown in Table 5. Unfiltered samples were taken of the supernatant after allowing the solids to settle. Soluble fluoride was measured using a fluoride ion specific electrode (ISE) after adding a TSAB buffer to the sample.

As shown in Table 5, the feed for experiment 1 contained 1,000 ppm HF. The pH was raised to 11.00 with lime, then samples were periodically taken of the supernatant. Note that the soluble fluoride content of the water dropped to 10 ppm after 5 min. The pH drifted downward to 8.35, reflecting consumption of lime by HF. Based on the result of experiment 2, the pH probably dropped to 8.35 after only 5 min, but it was not measured for 60 min.

Samples were taken and treated with various portions of coagulants and/or flocculants, as indicated in the last steps of experiment 1. KSP$^{®}$ 340 is a proprietary coagulant sold by Koch Microelectronic Service Co. (KMSC), while KSP$^{®}$ 107 is a flocculant. It is interesting to note that the soluble fluoride was reduced to 8.5 ppm from 9.5 ppm after treatment with the coagulant/flocculant combination. While **ESP** can model the chemistry and solubility of the system, the unit processes used are not capable of modeling the physical processes of precipitation, coagulation, or flocculation[10] (although such capability is being developed by OLI). Some real-world experimentation or experience is necessary to complete the connection between process simulation and the actual process.

Experiment 2 in Table 5 is an example of the real world variation from process simulation. The lowest fluoride concentration achievable was 26 ppm. While the true source of the error isn't known, it can be conjectured that rapid precipitation of CaF_2 coated the lime particles, making the lime unavailable for reaction with the low concentration of HF remaining in solution. Experiments 3 and 4 are additional examples of the requirement for use of coagulants and flocculants to reduce soluble fluoride to levels below 20 ppm. Although the lab results don't

Table 5

**Fluoride Removal from Synthetic HF Waste Using Lime in the Lab**

Exp.	HF conc. ppm	Wt. Lime added, g	pH	[F-] ppm	Comments
1	1,000	2.05	11.00		added lime to pH 11.0
				10	after 5 min. stirring
				10	after 30 min. stirring
			8.35	9.5	after 60 min. stirring
				8.6	after adding 10 ppm KSP 340 and 20 ppm KSP 107; very hazy
				8.5	after adding additional 10 ppm KSP 340 and 20 ppm KSP 107; light haze; fast settling floc
				8.1	fresh sample with 10 ppm KSP 340 and 20 ppm KSP 107; cloudy
2	10,000	21.71	11.00		added lime to pH 11.0
			8.32	39	after 5 min. stirring
				25	after 30 min. stirring
				32	after 60 min. stirring
				26	after adding 20 ppm KSP 340 and 300 ppm KSP 107; some floc, very cloudy supernatent
				29	fresh sample with 10 ppm KSP 340 and 200 ppm KSP 107; some floc with very cloudy supernatent
3	1,000	1.99	7.20		initial pH after lime = 9.0; added H2SO4 to 7.2
				26	after 5 min. stirring
				26	after 30 min. stirring
			8.45	25	after 60 min. stirring
				16	after adding 10 ppm KSP 340 and 10 ppm KSP 107; hazy, not clear, some floc
				14	after adding additional 20 ppm KSP 107; light haze; fast settling time
				15	fresh sample with 10 ppm KSP 340 and 20 ppm KSP 107; cloudy
				13	fresh sample with 10 ppm KSP 340 and 30 ppm KSP 107; near clear plus floc
4	10,000	18.99	8.10		added lime to pH 8
				38	after 5 min. stirring
				44	after 30 min. stirring
			7.93	41	after 60 min. stirring
				14	after adding 160 ppm KSP 107; very clear plus floc
				14	fresh sample with 10 ppm KSP 340 and 160 ppm KSP 107; slightly less clear than previous sample

exactly match the modeling results, modeling predicted the doubling of the fluoride concentration on lowering the pH from 11 to 8. The experiments confirmed that increase.

There is good agreement between prediction and experiment as far as the amount of lime necessary to produce the intended results. The process simulations predicted that between 1.85 and 1.90 g of lime would be used per g of HF in the system. In the laboratory between 1.9 and 2.1 g of lime was used per g of HF.

Hydrofluoric Acid Wastewater Treatment with CaCl$_2$

HF wastewater from semiconductor fabs often contains unusual components. In order to determine the usefulness of process simulation in such real-world situations, the calcium chloride treatment of a complex wastewater containing 1,000 ppm HF, 1,000 ppm sulfuric acid, 300 ppm acetic acid, 350 ppm NH$_4$OH, and 400 ppm phosphoric acid was modeled. The pH of the stream was arbitrarily set at 7.55 by adding 2,920 ppm of NaOH. Figure 2 is a PFD for the process simulation used.

Figure 2
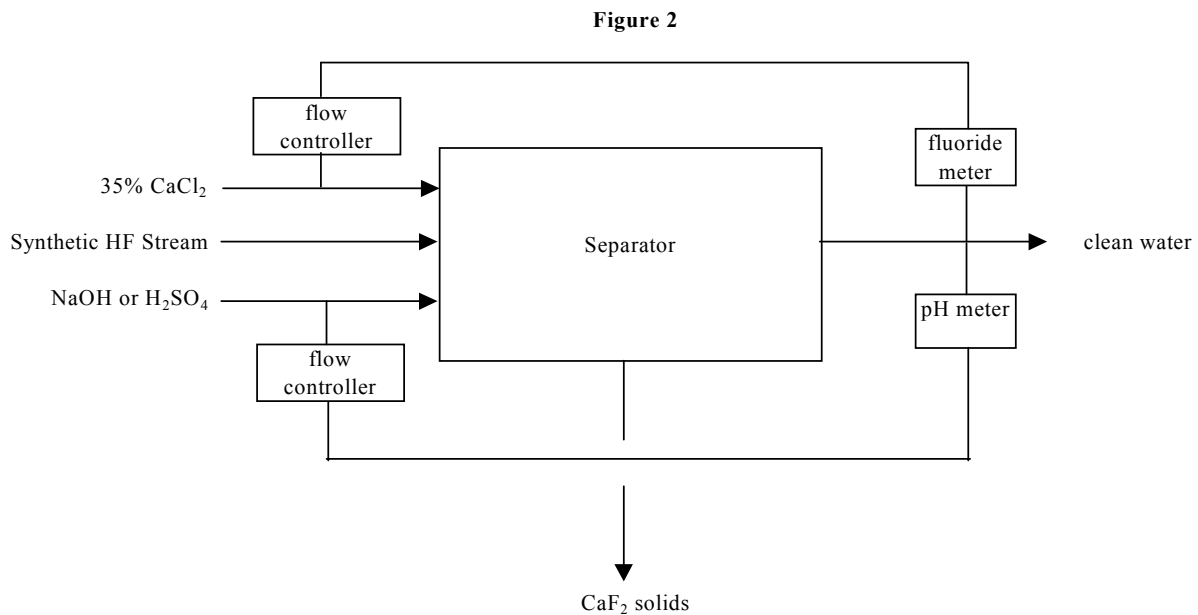
When using $CaCl_2$ two control loops are needed; one to control the $CaCl_2$ addition rate, and one to control the addition rate of the acid or base used to set the pH. The pH was set at either 3.5 or 8.0. Since the pH of the wastewater was 7.55, NaOH was added to raise the pH to 8.0, and H_2SO_4 was used to lower the pH to 3.5. As in the lime process, the pH control loop was used to achieve the desired pH target.

With **ESP** the concentration of components of the clean water can be monitored, and the information can be used to control chemical addition rates in order to meet fluoride discharge limits. In this case, the soluble fluoride content of the clean water was set at 7 ppm to give the facility breathing room below the typical 15-20 ppm discharge limit. The second control loop was used to set the $CaCl_2$ addition rate to meet the 7 ppm fluoride target.

The results of the process simulations at pH 8 or 3.5 are shown in Tables 6 and 7 respectively, with a summary in Table 8. At pH 8, the fluoride content of the clean water was about 7, composed of 0.52 ppm of NaF and 6.80 ppm of fluoride ion. The chloride content was 2,235 ppm, the acetic acid content was 0.12 ppm, the sulfate content was 900 ppm and the ammonia content was 7.67 ppm. The precipitated solid contained 24% $Ca_3(PO_4)_2$ and 76% CaF_2.

Contrast the results at pH 8 with the results at pH 3.5. The fluoride content was again about 7 ppm, composed of 2.04 ppm HF, 0.35 ppm NaF, and 4.89 ppm fluoride ion. The chloride content was 1,882 ppm, the acetic acid content was 277 ppm, the sulfate content was 1,270 ppm, and the ammonia content was less than 0.01 ppm. The differing results reflect the equilibrium compositions at the two pH values.

Table 6

Treatment Of HF Wastewater with CaCl₂ at pH 8

Syn. HF Component	ppm
Water	994,030
HF	1,000
H₂SO₄	1,000
H₃PO₄	400
Acetic Acid	300
NH₄OH	350
NaOH	2,920

Stream	Synthetic HF	CaCl2	NaOH	clean waste	precipitate
Phase	Aqueous	Aqueous	Aqueous	Aqueous	Solid
Temperature, C	25.00	25.00	25.00	25.18	25.18
Pressure, atm	1.00	1.00	1.00	1.00	1.00
pH	7.55	5.42	14.45	8.05	
Total mol/min	26,240	217.58	52.42	26,470	12.70
Flow Units	ppm	ppm	ppm	ppm	ppm
H2O	995,525	650,000	900,000	994,499	
ACETACID	0.38			0.12	
HF	0.03			0.00	
NH3	2.47			7.67	
NAACET	12.90			13.86	
NAF	65.35			0.52	
NH4ACET	3.33			3.16	
OHION	0.01	0.00	42,521.30	0.03	
FION	920.00			6.80	
H2PO4ION	66.03			0.23	
HP2O7ION	0.02			0.00	
HPO4ION	326.38			3.61	
NA2FION	0.06			0.00	
NAION	1,633.51		57,478.80	1,767.32	
NASO4ION	28.18			29.64	
NH4ION	169.75			163.11	
NH4SO4ION	44.27			41.00	
ACETATEION	282.76			278.86	
PO4ION	0.02			0.00	
SO4ION	919.43			900.40	
CAION		126,390		32.44	
CAOHION		0.02		0.00	
CLION		223,609		2,234.66	
CAACET2				0.09	
CASO4				16.10	
CAACETION				1.24	
CAPO4ION				0.14	
CA3PO42					244,463
CAF2					755,537
Total g/min	473,550	4,777.67	953.88	478,070	1,213.85
Volume, gal/min	125.00	0.94	0.23	126.21	0.10
Enthalpy, Btu/min	-7.11E+06	-5.91E+04	-1.40E+04	-7.17E+06	-1.75E+04
Density, g/gal	3,788.44	5,059.58	4,143.51	3,788.06	12,039.50
Osmotic Pres, atm	3.16	932.43	169.76	3.54	
E-Con, 1/ohm-cm	7.20E-03	1.73E-01	3.09E-01	9.19E-03	
E-Con, cm2/ohm-mol	4.72E+01	4.10E+01	1.13E+02	9.81E+01	
Abs Visc, cP	9.08E-01	4.86E+00	1.59E+00	8.97E-01	
Rel Visc	1.02E+00	5.45E+00	1.78E+00	1.01E+00	
Ionic Strength	9.39E-02	1.46E+01	2.78E+00	9.83E-02	

Table 7

Treatment Of HF Wastewater with CaCl$_2$ at pH 3.5

Syn. HF Component	ppm
Water	994,030
HF	1,000
H$_2$SO$_4$	1,000
H$_3$PO$_4$	400
Acetic Acid	300
NH$_4$OH	350
NaOH	2,920

Stream	Synthetic HF	CaCl2	H$_2$SO$_4$	clean waste	precipitate
Phase	Aqueous	Aqueous	Aqueous	Aqueous	Solid
Temperature, C	25.00	25.00	25.00	25.18	25.18
Pressure, atm	1.00	1.00	1.00	1.00	1.00
pH	7.55	5.42	-0.03	3.49	
Total mol/min	26,240	183.55	109.39	26,495	11.75
Flow Units	**ppm**	**ppm**	**ppm**	**ppm**	**ppm**
H2O	995,525	650,000	900,000	994,105	
ACETACID	0.38			277.41	
HF	0.03			2.04	
NH3	2.47			0.00	
NAACET	12.90			0.84	
NAF	65.35			0.35	
NH4ACET	3.33			0.21	
H3PO4	0.00			12.73	
OHION	0.01	0.00	0.00	0.00	
FION	920.00			4.89	
H2P2O7ION	0.00			0.02	
H2PO4ION	66.03			370.69	
HION	0.00	0.00	1,188.25	0.42	
HP2O7ION	0.02			0.00	
HPO4ION	326.38			0.16	
HSO4ION	0.00		83,511.80	16.54	
NA2FION	0.06			0.00	
NAION	1,633.51			1,652.23	
NASO4ION	28.18			38.65	
NH4ION	169.75			168.77	
NH4SO4ION	44.27			59.28	
ACETATEION	282.76			18.14	
PO4ION	0.02			0.00	
SO4ION	919.43		15,299.90	1,269.52	
CAION		126,390		64.34	
CAOHION		0.02		0.00	
CLION		223,610		1,882.42	
CASO4				43.77	
CAACETION				0.16	
CAH2PO4ION				11.46	
CAF2					1,000,000
Total g/min	473,550	4,030.33	2,097.33	478,770	917.15
Volume, gal/min	125.00	0.80	0.52	126.33	0.08
Enthalpy, Btu/min	-7.11E+06	-4.99E+04	-3.02E+04	-7.18E+06	-1.38E+04
Density, g/gal	3,788.44	5,059.58	4,031.08	3,789.95	12,043.30
Osmotic Pres, atm	3.16E+00	9.32E+02	6.04E+01	3.35E+00	
E-Con, 1/ohm-cm	7.20E-03	1.73E-01	4.37E-01	8.91E-03	
E-Con, cm2/ohm-mol	4.72E+01	4.10E+01	4.03E+02	1.01E+02	
Abs Visc, cP	9.08E-01	4.86E+00	1.13E+00	8.98E-01	
Rel Visc	1.02E+00	5.45E+00	1.27E+00	1.01E+00	
Ionic Strength	9.39E-02	1.46E+01	1.49E+00	1.00E-01	

Table 8

Summary of Modeling Results

	pH = 8.0	pH = 3.5
clean water [HF], ppm	0.00	2.04
clean water [NaF], ppm	0.52	0.35
clean water [F⁻], ppm	6.80	4.89
clean water [Cl], ppm	2,235	1,882
clean water [AcOH], ppm	0.12	277
clean water [SO_4], ppm	900	1,270
clean water [NH_3], ppm	7.67	0.01
$Ca_3(PO_4)_2$, % of solids	24.00	0.00
CaF_2, % of solids	76.00	100.00

Since soluble calcium was removed from the reaction mixture at pH 8 by the precipitation of the $Ca_3(PO_4)_2$, additional $CaCl_2$ had to be added to compensate, and the resulting chloride content of the clean water at pH 8 was higher than at pH 3.5. This demonstrates that subtle changes in pH could have far reaching effects on effluent quality and process cost.

Laboratory Test of Fluoride Waste CaCl₂ Treatment

Work was done in the laboratory to back-up the $CaCl_2$ process simulations. The results are shown in Table 9. With the simple experimental set-up as described in the previous section it was not possible to exactly duplicate the simulated process in the lab. Instead of simultaneously adjusting the pH and the $CaCl_2$ addition rate, a predetermined amount of $CaCl_2$ was added, and the pH was adjusted either before or after the addition (or both). The idea was to add about 1.5 equivalents of $CaCl_2$, based on HF content. No adjustments were made for the presence of the other acidic components, which can also form salts with calcium.

In experiment 1, the $CaCl_2$ was added to the synthetic HF wastewater without any prior pH adjustment. The soluble fluoride content was reduced to 190 ppm after 30 min, and the pH was 2.0. After adjusting to pH 8.1, the soluble fluoride dropped to 41 ppm. The fluoride content dropped below 20 ppm only after letting the reaction mixture settle for 12 min.

Table 9

Fluoride Removal from Synthetic HF Waste By Lab Treatment with CaCl$_2$

Exp.	HF conc. ppm	Wt. 35% CaCl$_2$ added, g	pH	[F-] ppm	Comments
1	1,000 HF +	12.50			added CaCl$_2$ (59 mole % XS) to synthetic HF waste w/o pH adjustment
	1,000 H$_2$SO$_4$ +			190	after 5 min. stirring
	300 AcOH +		2.0	190	after 30 min. stirring
	350 NH$_4$OH +		8.1	41	5 min. after adjusting pH to 8.1 with NaOH
	400 H$_3$PO$_4$			40	30 min after adjusting pH to 8.1
			7.8	41	60 min after adjusting pH to 8.1
			7.1	15	after letting settle for 12 min.
2	1,000 HF +	12.50			adjusted pH to 8.0 before adding 59 mole % XS CaCl$_2$
	1,000 H$_2$SO$_4$ +			46	after 5 min. stirring
	300 AcOH +			47	after 30 min. stirring
	350 NH$_4$OH +		5.1	48	after 60 min. stirring
	400 H$_3$PO$_4$		8.0	66	5 min. after adjusting pH back to 8.0 with NaOH
				66	30 min after adjusting pH back to 8.0
			7.8	62	60 min after adjusting pH back to 8.0, with 12 min. settling time
3	1,000 HF +	24.80			added 215 mole % XS CaCl$_2$ w/o pH adjust
	1,000 H$_2$SO$_4$ +			82	after 5 min. stirring
	300 AcOH +		1.8	76	after 30 min. stirring
	350 NH$_4$OH +		8.1	9	5 min. after adjusting pH to 8.1 with NaOH
	400 H$_3$PO$_4$			8	30 min. after adjusting pH to 8.1
			7.8	7	60 min. after adjusting pH to 8.1
				7	after 2 hr of settling
4	1,000 HF +	37.20			added 473 mole % XS CaCl$_2$ w/o pH adjust
	1,000 H$_2$SO$_4$ +			71	after 5 min. stirring
	300 AcOH +		1.8	65	after 30 min. stirring
	350 NH$_4$OH +		8.0	8	5 min. after adjusting pH to 8.0 with NaOH
	400 H$_3$PO$_4$			6	30 min. after adjusting pH to 8.0
			7.7	6	60 min. after adjusting pH to 8.0
				5	after 2 hr of settling
5	1,000 HF +	12.50	3.5		pH adjusted with NaOH before adding the CaCl2
	1,000 H$_2$SO$_4$ +		2.2		pH 2.2 after adding the 59 mole % excess CaCl2; adjusted to 3.5 with NaOH
	300 AcOH +		3.3	16	after 5 min. stirring; adjusted pH back to 3.6
	350 NH$_4$OH +		3.4	14	after 30 min. stirring
	400 H$_3$PO$_4$		3.4	13	after 60 min. stirring
			3.4	13	after 4.5 hr stir + standing
			3.4	12	after filtration through 0.2 micron filter

In contrast, the pH of the feed to experiment 2 was adjusted to 8.0 before adding the CaCl$_2$. The fluoride content immediately dropped to 46 ppm. The 35% CaCl$_2$ has a pH around 5, and this caused the pH of the reaction mixture to drop to 5.1 after 60 min. Readjustment of the pH to 8.0 caused an increase in the soluble fluoride content to 66 ppm. Even on standing, the soluble fluoride did not drop below 62 ppm.

In experiments 3 and 4 a large excess of $CaCl_2$ was added without prior pH adjustment of the feed. In both cases, soluble fluoride concentrations below 10 ppm were not achieved until the pH of the reaction mixture was raised to 8.0.

In experiment 5, the pH of the feed was adjusted to 3.5 using NaOH. The pH was readjusted to 3.5 after adding the excess $CaCl_2$. The soluble fluoride content was 16 ppm, dropping to 13 ppm after stirring for 60 min. This is a better result than that obtained under the same conditions at pH 8 of experiment 1, which required settling before achieving the low soluble fluoride content.

At pH 3.5, **ESP** predicted that 1.08 equivalents, or 8 mole % excess, $CaCl_2$ would be needed to produce a soluble fluoride content of 7 ppm. In the lab 1.59 eq. $CaCl_2$, or 59 mole % excess, only reduced the soluble fluoride content to 13 ppm. At pH 8, **ESP** predicted that 1.28 eq. $CaCl_2$, 28 mole % excess, would be required to achieve the target soluble fluoride concentration of 7 ppm while the lab work indicated that a much larger excess of 3.15 eq., or 215 mole % excess, was necessary. Recall that the **ESP** calculations were based on strict thermodynamics, with no kinetic factors taken into consideration. The difference between prediction and lab can then be attributed to the simulation being in thermodynamic equilibrium. Given enough time, the lab results probably would have closely resembled the simulation results. The conclusion is that retention time, and issues associated with retention time, will be a very important factor in designing a full-size system. It is possible to factor kinetics into a process simulation, but that is beyond the intentions of this paper. Piloting the treatment of the wastewater would be the most valuable exercise.

Neutralization of Dilute Acid Wastewater

Most of the time, the analysis of a wastewater stream only indicates the concentrations of anions and cations, and a few other parameters. How are these components put together, i.e. is "sulfate" present as sodium sulfate or sulfuric acid? If the pH is changed or a treatment chemical is added, what compositional changes occur?

Table 10

Neutralization of Dilute Acid With Lime

Stream	Dilute Acid	manipulated slurry		neutral water	Dilute Acid	manipulated slurry		neutral water
Phase	Aqueous	Aqueous	Solid	Aqueous	Aqueous	Aqueous	Solid	Aqueous
Temperature, C	25.00	25.00	25.00	25.01	25.00	25.00	25.00	25.01
Pressure, atm	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
pH	3.17	12.39		7.94	3.17	12.39		7.94
Total mol/min	20,946.70	11.06	0.14	20,958.30	20,946.70	11.06	0.14	20,958.30
Flow Units	**wtfrac**	**wtfrac**	**wtfrac**	**wtfrac**	**ppm**	**ppm**	**ppm**	**ppm**
H2O	1.00E+00	9.99E-01		1.00E+00	999,944	998,755		999,929
H2F2	3.19E-16			3.77E-25	0.00			0.00
H2SO4	1.77E-20			5.03E-30	0.00			0.00
HCL	1.10E-14			1.84E-19	0.00			0.00
HF	4.05E-07			1.39E-11	0.40			0.00
HNO3	1.87E-10			3.13E-15	0.00			0.00
NH3	5.47E-12			3.08E-07	0.00			0.31
SO3	1.87E-24				0.00			
KHSO4	1.20E-13			2.01E-18	0.00			0.00
NAF	1.62E-11			3.29E-11	0.00			0.00
NANO3	3.74E-12			3.69E-12	0.00			0.00
CASO4	1.91E-08			5.96E-07	0.02			0.60
NH4NO3	1.49E-08			1.40E-08	0.01			0.01
KCL	3.10E-12			3.06E-12	0.00			0.00
OHION	2.66E-13	5.18E-04		1.59E-08	0.00	517.72		0.02
CAION	4.81E-07	5.47E-04		1.53E-05	0.48	546.62		15.31
CANO3ION	2.52E-10			7.84E-09	0.00			0.01
CAOHION	1.55E-16	1.81E-04		2.89E-10	0.00	180.58		0.00
CLION	2.78E-05			2.78E-05	27.80			27.78
FION	3.66E-07			7.50E-07	0.37			0.75
HF2ION	3.69E-12			2.60E-16	0.00			0.00
HION	7.08E-07	5.00E-16		1.20E-11	0.71	0.00		0.00
HSO4ION	6.94E-07			1.18E-11	0.69			0.00
KION	2.71E-07			2.71E-07	0.27			0.27
KSO4ION	7.58E-10			7.58E-10	0.00			0.00
NA2FION	7.63E-18			1.55E-17	0.00			0.00
NAION	6.46E-07			6.45E-07	0.65			0.65
NASO4ION	3.75E-10			3.75E-10	0.00			0.00
NH4ION	7.10E-06			6.77E-06	7.10			6.77
NH4SO4ION	6.13E-08			5.85E-08	0.06			0.06
NO3ION	5.71E-06			5.70E-06	5.71			5.70
CAFION	8.60E-13			5.50E-11	0.00			0.00
SO4ION	1.21E-05			1.24E-05	12.11			12.39
CAOH2			1.00E+00				1,000,000	
Total g/min	377,370	199.24	10.23	377,570	377,370	199.24	10.23	377,570
Volume, gal/min	100.00	0.05	0.00	100.05	100.00	0.05	0.00	100.05
Enthalpy, Btu/min	-5.67E+06	-3.00E+03	-1.29E+02	-5.68E+06	-5.67E+06	-3.00E+03	-1.29E+02	-5.68E+06
Density, g/gal	3,773.60	3,778.97	8,478.56	3,773.68	3,773.60	3,778.97	8,478.56	3,773.68
Osmotic Pres, atm	0.05	1.01		0.04	0.05	1.01		0.04
E-Con, 1/ohm-cm	3.57E-04	6.33E-03		1.55E-04	3.57E-04	6.33E-03		1.55E-04
E-Con, cm2/ohm-mol	2.59E+02	8.94E+00		8.72E+01	2.59E+02	8.94E+00		8.72E+01
Abs Visc, cP	8.91E-01	9.00E-01		8.91E-01	8.91E-01	9.00E-01		8.91E-01
Rel Visc	1.00E+00	1.01E+00		1.00E+00	1.00E+00	1.01E+00		1.00E+00
Ionic Strength	1.29E-03	4.41E-02		1.69E-03	1.29E-03	4.41E-02		1.69E-03

As an example, an analysis of a dilute acid wastewater showed 100 ppm sulfate, 50 ppm chloride, 5 ppm fluoride, 20 ppm nitrate, 10 ppm sodium, 20 ppm ammonium, 5 ppm potassium, and 2 ppm calcium. The measured pH was 3.17. Given these ionic components, what molecular species were actually present in the water, and what happened when the water was neutralized to pH 8 using dilute lime?

An application called **WaterAnalyzer** in the OLI suite of programs was used to charge balance the analysis, and to output a stream containing the molecular species corresponding to the anions and cations present in the water. This stream was then used to feed a neutralization process in **ESP**, where the flow of 5% lime was controlled using a pH controller in order to achieve 8 pH. The data is presented in Table 10.

Note that the Dilute Acid feedstock contained 33 components including water. Some of these components were neutral species such as H_2F_2, H_2SO_4, and HCl, and some were ionic species such as hydroxide anion and hydrogen cation. As expected in a pH change, neutralization produced exponential changes in the concentrations of six components, as summarized in Table 11.

Table 11

Neutralization of Dilute Acid

	dilute acid	neutral water
[HF], ppm	0.40	0.000014
[NH3], ppm	0.0000055	0.31
[CaSO4], ppm	0.02	0.60
[Ca++], ppm	0.48	15.31
[H+], ppm	0.71	0.000012
[HSO4-], ppm	0.69	0.000012

While the simulation results are not earth shattering, they illustrate the huge changes in composition which can occur on carrying out simple pH changes. The simulation becomes more valuable as the complexity of the system increases. For instance, if the ammonium concentration of the wastewater was hundreds of ppm, the neutral water could evolve gaseous ammonia at

levels above safe exposure limits, necessitating a closed system. With process simulation, one could examine myriad pH and concentration scenarios before designing the final system.

Wastewater from CMP Operations

Chemical mechanical planarization (CMP) is a new technology for producing smooth surfaces on semiconductor chips. An aqueous slurry of silica or alumina is used along with a rotating CMP pad to "wet sand" metal or oxide surfaces. The wastewater from CMP operations can contain high concentrations of solids, typically 1,000 ppm, and other components removed from the chip. Clarification or filtration is used to remove the solids if the POTW has limitations on solids discharge. In order to design an acceptable process, the solubility of the silica, alumina, and other components under different conditions of pH, temperature, etc., should be known. In this section the water solubility of alumina and silica at various pH values will be determined (process simulation of clarification or filtration will be the subject of a future publication). This information can be used to adjust the pH of the wastewater to its optimal value for removal of the solids.

The chemistry of silica is quite complex[11] and cannot begin to be addressed by this paper. The chemistry of alumina is simpler but still formidable[12]. The combination of the two can produce alumino-silicates of indeterminate structure. Process simulation can be used to point out potential operating ranges; each situation would have to be optimized based on its particular components and conditions.

A simple wastewater containing only 1,000 ppm of SiO_2 and 1,000 ppm of $Al(OH)_3$ was titrated between pH 2 and pH 12 using either NaOH or H_2SO_4 as titrants. Equilibrium calculations in OLI's **Express Calculate** application determined that the natural pH of the mixture was 6.05. The pH of the system was varied in 0.2 pH increments, using H_2SO_4 to lower the pH below the natural pH, and NaOH to raise the pH above the natural pH. At each pH value, the equilibrium composition of the mixture was determined. The data is presented in Chart 1.

Chart 1
Titration of Silica/Aluminum Hydroxide Mixture
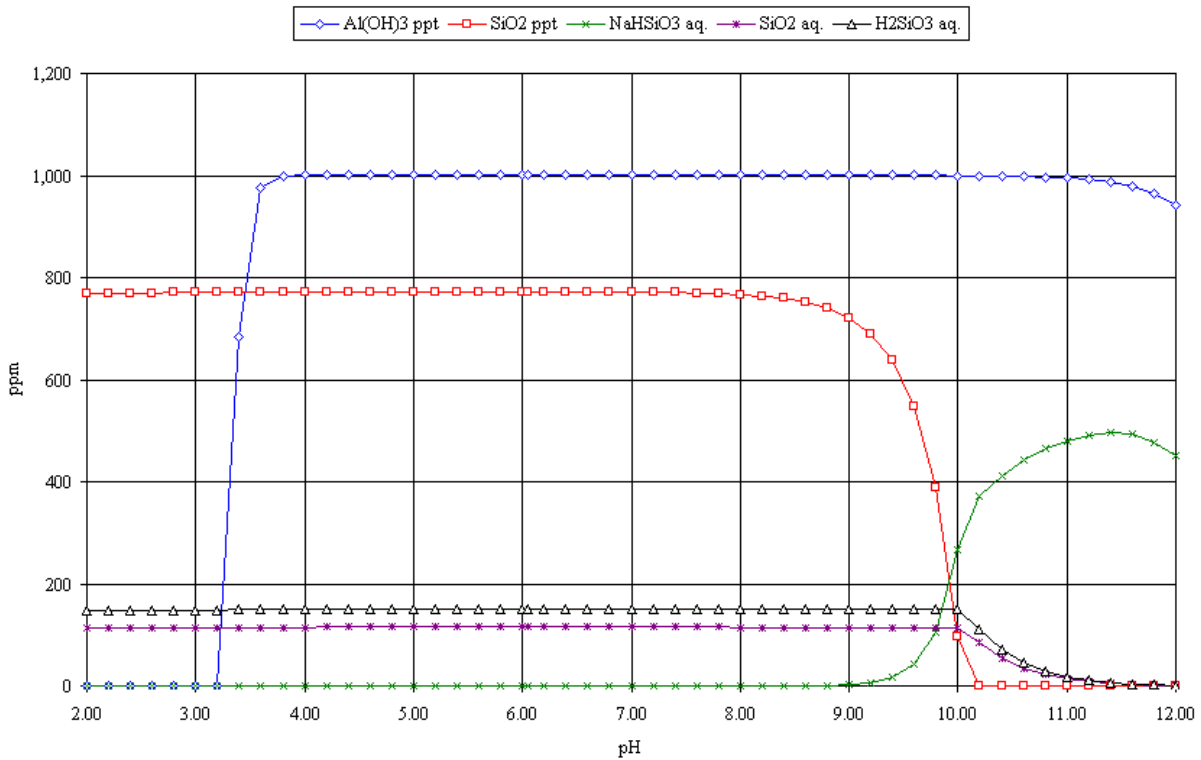
As Chart 1 indicates, from pH 2 to pH 8, SiO_2 was present mainly as three components: precipitated SiO_2; aqueous SiO_2; and aqueous hydrated silica H_2SiO_3. Filtration or clarification would only remove about 80% of the silica, since the remainder was water soluble. As the pH rose above 8 the precipitated SiO_2 began to dissolve and $NaHSiO_3$ started appearing in solution. As the pH rose past 10 the concentrations of aqueous SiO_2 and H_2SiO_3 started dropping while other components (not shown) started increasing in concentration.

Contrary to the silica titration curve, from pH 4 to about 10.5 the concentration of precipitated $Al(OH)_3$ was constant, with very little if any water solubility. Dropping the pH below 3.5 produced a sharp decrease in the amount of solid $Al(OH)_3$ as it was converted to soluble $Al_2(SO_4)_3$. At high pH, the $Al(OH)_3$ did not start to dissolve until the pH increased to 11.5.

There are many conceivable ways this data could be used to help design a wastewater treatment system. As an example, if one wanted to separate the SiO_2 from the $Al(OH)_3$, then the pH could

be set at 2.5, and the solid silica could be removed from the dissolve $Al(OH)_3$. Or conversely, the pH could be set at 10.25 and the solid $Al(OH)_3$ could be filtered away from the dissolved silica.

Treatment of Cu CMP Wastewater

Wastewater from copper CMP tools contains from 5 to 100 ppm soluble copper, usually in the form of Cu^{+2} (cupric ion). The slurries used can be either silica or alumina based. Depending on the slurry manufacturer, other components such as oxidizers or chelants can be present. A typical component in slurries is ammonia, which can form copper chelation compounds.

The discharge limitations for copper vary by location, but are generally <1.50 ppm. One method of treating copper-containing wastewater is to raise the pH to form cupric hydroxide ($Cu(OH)_2$), which precipitates from solution, and can be removed along with other solids present in the system by clarification or filtration. What is the optimal pH range for precipitation of $Cu(OH)_2$? **Express Calculate** was used to complete a pH survey. A wastewater feed containing 154 ppm $Cu(OH)_2$ (equivalent to 100 ppm Cu^{+2}) was titrated with either NaOH or H_2SO_4. Below the natural pH of 6.05, H_2SO_4 was used to lower the pH. Above 6.05 pH, NaOH was used to raise the pH. The data is presented in Chart 2.

Below about pH 4.5 all of the Cu^{+2} was in solution. As the system approached pH 6, the Cu^{+2} started precipitating as $Cu(OH)_2$. At pH 8 all of the copper had precipitated from solution. The optimal pH for removing copper from the wastewater via clarification or filtration was therefore at or above 8.

When 1,000 ppm ammonia was added to the system, the situation changed drastically, as shown in Chart 3. Ammonia will form cupric ion complexes above pH 6. These complexes have the molecular formulas $Cu(NH_3)_2^{+2}$, $Cu(NH_3)_3^{+2}$, $Cu(NH_3)_4^{+2}$, and $Cu(NH_3)_5^{+2}$. The concentrations of each complex depend on the relative concentrations of copper and ammonia and the pH. The higher the concentration of ammonia and the higher the pH, the more of the tetra- and

Chart 1
**Precipitation of Cupric Hydroxide**
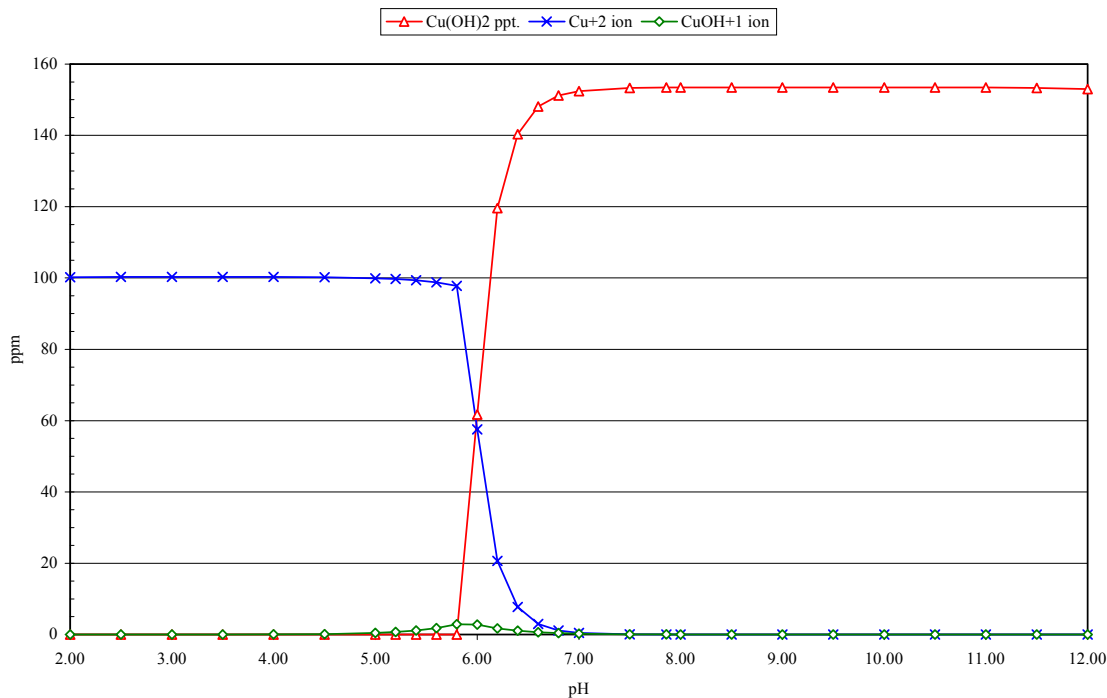
penta-ammonia complexes will form. Contrary to the situation with the non-complexed $Cu(OH)_2$, the ammonia complexes are very water soluble

As Chart 3 indicates, in the presence of a large amount of ammonia, substantial amounts of $Cu(NH_3)_2^{+2}$, $Cu(NH_3)_3^{+2}$, and $Cu(NH_3)_4^{+2}$ were formed. The maximum concentration of $Cu(NH_3)_4^{+2}$ occurred at about pH 9.4. The process will fail to meet discharge limitations at that pH. Above pH 9.4, the concentration of $Cu(NH_3)_4^{+2}$ declined and the concentration of $Cu(OH)_2$ increased, so that a pH of about 12 would yield optimal copper removal via precipitation of $Cu(OH)_2$.

In a real world example, the process simulation software was used to support the design and commercialization of a Cu CMP wastewater treatment process for which multiple process patent applications have been filed. The time span from conception to commercialization was about 6 months.

Chart 3
Precipitation of Cupric Hydroxide In Presence of 1,000 ppm NH3
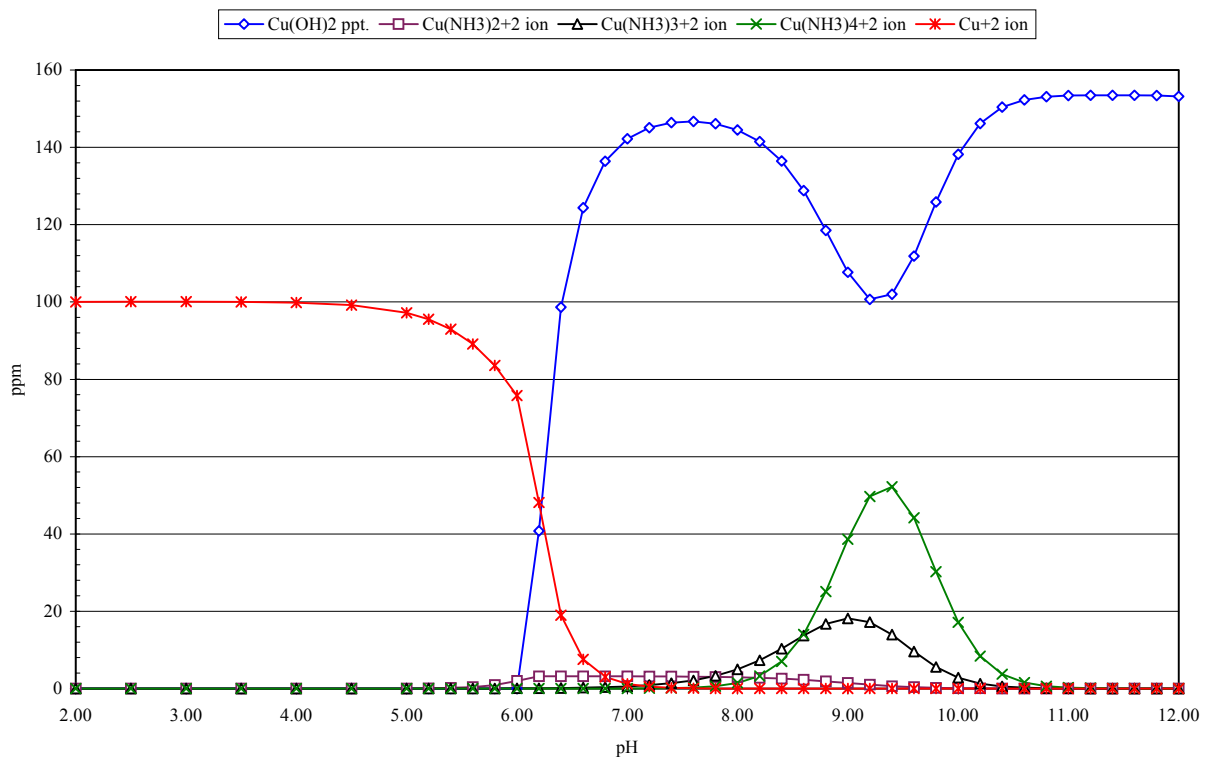
Conclusion

It has been shown that process simulation software can make predictions that are very similar to the results of real world experiments. In addition, it has been shown that the data generated leads to identification of problem areas and pitfalls in process design. The use of process simulation software to guide the development of wastewater treatment processes will enable faster turn-around times at lower overall cost than lab development. Due to the ability to ask the question "what if?" the systems designed will be more robust. Adaptation of existing systems to new conditions and components will be easier since many different parameters can be explored in a matter of hours rather than days or weeks. Troubleshooting of operating systems can be facilitated by process simulation software.

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Biography

Dustin K. James has been working as Chemistry and Technology Manager in the Water Reclaim Group of KMSC for 17 months. Prior he was employed with Koch Specialty Chemical Co., first as a Principal Research Chemist in process and product development at the R&D lab in Wichita, Kansas, for 9 ½ years, then as the Technology Exploitation Manager in Houston, Texas, for 1 year. Dustin is a co-inventor on three granted process patents, and three additional patent applications. He received his Bachelor of Science degree in Chemistry from Southwestern University in Georgetown, Texas, and his Ph.D. in organic synthetic chemistry from The University of Texas at Austin. Prior to working for Koch Industries, Inc., Dustin was employed by Norwich Eaton Pharmaceuticals (a subsidiary of Procter and Gamble) in Norwich, New York, as a Staff Scientist in the Process Development lab. He is a member of the American Chemical Society and TAPPI.

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References

[1] *International Technology Roadmap for Semiconductors 1998 Update*, Sponsored by the Semiconductor Industry Association

[2] AspenTech's products include Aspen Plus® and BATCHFRAC® for doing process design, among a list of 20 or more software packages for design, control, and optimization. More information can be obtained from their web page at http://www.aspentech.com/index.htm.

[3] Simulation Science, Inc.'s products include the Process Engineering Suite™ of PRO/II, HEXTRAN, DATACON, INPLANT, and VISUAL FLOW. More information can be obtained from their web page at http://www.simsci.com/index_old.htm.

[4] See Pacific Simulations, Inc.'s web page at http://www.pacsim.com/default.shtml.

[5] J.M. Spooner "Review of Computer Process Simulation in Industrial Pollution Prevention" Report (1994), EPA/600/R-94/128; Order No. PB95-154886, 56 pp. Avail.: HTIS

[6] Details and contact information can be found at OLI Systems' web page http://www.olisystems.com/.

[7] Information about French Creek Software's programs can be found on their web page at http://www.frenchcreeksoftware.com/.

[8] The OLI engine framework is based upon:

- "the revised Helgeson equation of state for predicting the partial molar standard-state thermodynamic properties of all species, including organics, in water;"

- "the Bromley-Zematis framework for the prediction of excess thermodynamic properties of ions;"

- "the Pitzer and Setschenow formulation for the prediction of excess thermodynamic properties calculation of molecular species in water; and"

- "the Enhanced SRK equation of state for the prediction of vapor and non-aqueous, liquid phase themodynamic properties. This enhanced equation of state applies to organics which are sparingly soluble in water, and which form a second liquid phase which is largely ideal."

Jim Berthold "A Guide to Using ESP" OLI Systems, Inc., 1999, Chapter 1, page 3.

[9] Punnchalee Laothumthut, *Chemistry and Chemical Process Studies of Fluoride Removal in a Silicon Wafer Manufacturing Wastewater Treatment Plant*, M.S.Thesis, Oregon State University, 20 March 1996.

[10] Yong H. Kim, Ph.D., *Coagulants and Flocculants: Theory and Practice*, Tall Oaks Publishing, Littleton, CO, 1995.

[11] Ralph K. Iler; *The Chemistry of Silica: Solubility, Polymerization, Colloid, and Surface Properties, and Biochemistry*, John Wiley and Sons, New York, 1979.

[12] Garrison Sposito, Ph.D., Editor, *The Environmental Chemistry of Aluminum 2nd Edition*, Lewis Publishers, Boca Raton, Florida, 1996.