Purification of Wastewater from the Microelectronics Industry

Background

The amount of wastewater produced by the semiconductor industry has recently come under strong environmental scrutiny. Microelectronic processes consume millions of gallons of water daily to rinse microscopic dirt and chemicals from the surface of chips. Land disposal of these types of waste are prohibited unless they are pretreated to Best Demonstrated Available Technology (BDAT) standards. Current emphasis is being placed on reducing the amount of waste produced. However, until a more suitable means of production is established, the waste stream must be treated.

There are actually several different waste streams that are produced throughout microelectronics manufacturing processes. When considered individually, these wastes are fairly typical and easily treatable. However, due to ongoing research to determine the best way to treat the waste, the individual streams are sometimes combined and stored. This project addresses one potential treatment train applicable to the combined mixed waste stream.

Environmental Significance

treatment of a waste stream

possible recycle or sale of recovered materials

Process Description

The PFD is attached. The waste stream, consisting of water contaminated with small amounts of Cu^{+2}, Sn^{+2}, Pb^{+2}, HF, methyl methacrylate, methanol, and acetone, enters the process as Stream 1. The waste undergoes an ion-exchange process in A-401 A/B where low concentrations of the three metals are effectively removed. The ion-exchange process consists of two columns, one in use and one being regenerated. The regenerant for the column consists of nitric acid. The exact concentration of the regeneration solution has not been determined; however, a 1 M solution of HNO_3 should be suitable. It is known that 250 moles of the nitric acid are required to regenerate the column. This is based on the column capacity, which has been sized for a one-day loading time followed by up to a one-day regeneration time. The regeneration effluent from the column, Stream 4, contains the metals originally removed from the wastewater and will be sent to an electrowinner to recover the metals. The ion exchange column and the electrowinner complement each other, as the ion exchange column is effective in removing low-level concentrations of ions while the electrowinner is more effective in removing high concentrations of metals. The electrowinning process produces a low volume of scrap metal which can be easily landfilled rather than large quantities of sludge which are more difficult to dispose of.

Once the metals have been removed, the water stream, Stream 3, is fed to R-401. This reactor is used to add lime to the wastewater to neutralize the HF resulting in the formation of calcium fluoride. The CaF is a solid and can be easily removed from Stream 9 through a filtration process. The particulates are removed from the water in F-401, preparing the waste for the separations section of the process.

The waste enters the separations section of the process as Stream 10, containing only the organics. The first distillation column, T-401, is used to separate acetone and methanol from the water and methyl methacrylate. Then, T-402 is used to separate the acetone and methanol in Stream 12, which exit the system as Streams 14 and 15, respectively. The methyl methacrylate is removed from the water in A-402 A/B using carbon adsorption. The “clean water” exits the system as Stream 16.

The carbon in the column is regenerated off-site using steam.

Necessary Information and Simulation Hints

Chemcad was used to simulate the majority of the process using the SRK model. The ion-exchange column was modeled as a component separator and size was calculated by hand assuming a capacity of 200 meq/100 g and a bulk density of 800 g/L. The reactor was sized for a 10 minute residence time at a flow rate of 0.0067 m^3/s. The filter was assumed to remove all solids while allowing 99% of the liquid to continue on to the rest of the process. The two distillation columns were designed on Chemcad. The carbon adsorption column was also simulated as a component separator and sized by hand. The Freundlich isotherm model was used to determine the amount of carbon required. The following parameters were used[1]

$$\frac{x}{m} = K_F C_e^{1/n}$$

where

x = mass of methyl methacrylate

m = mass of carbon

K_F = Freundlich adsorption constant = 1.3

C_e = concentration of methyl methacrylate in solution at equilibrium

n = Freundlich exponent = 0.58

Since parameters for methyl methacrylate are not available, the parameters used are the averages of the values for acrolein and acrylonitrile.[1] Once the mass of carbon required was determined, the size of the column was calculated assuming a bulk density of 500 kg/m^3. The carbon was assumed to be regenerated by the manufacturer.

Equipment Descriptions

A-401 A/B Ion Exchange Columns

R-401 Lime Reactor

F-401	Rotary Vacuum Filter
T-401	Water Column (acetone/methanol from water/methyl methacrylate)
E-401	Water Column Condenser
E-402	Water Column Reboiler
V-401	Water Column Reflux Drum
P-401 A/B	Water Column Reflux Pumps
T-402	Acetone Column
E-403	Acetone Column Condenser
E-404	Acetone Column Reboiler
V-402	Acetone Column Reflux Drum
P-402 A/B	Acetone Column Reflux Pumps
A-402 A/B	Carbon Adsorber
EW-401	Electrowinning Unit

References

1. Montgomery, James M., *Water Treatment. Principles and Design*, Wiley-Interscience, New York, 1985, p. 186.

Stream Table for Wastewater Purification Process

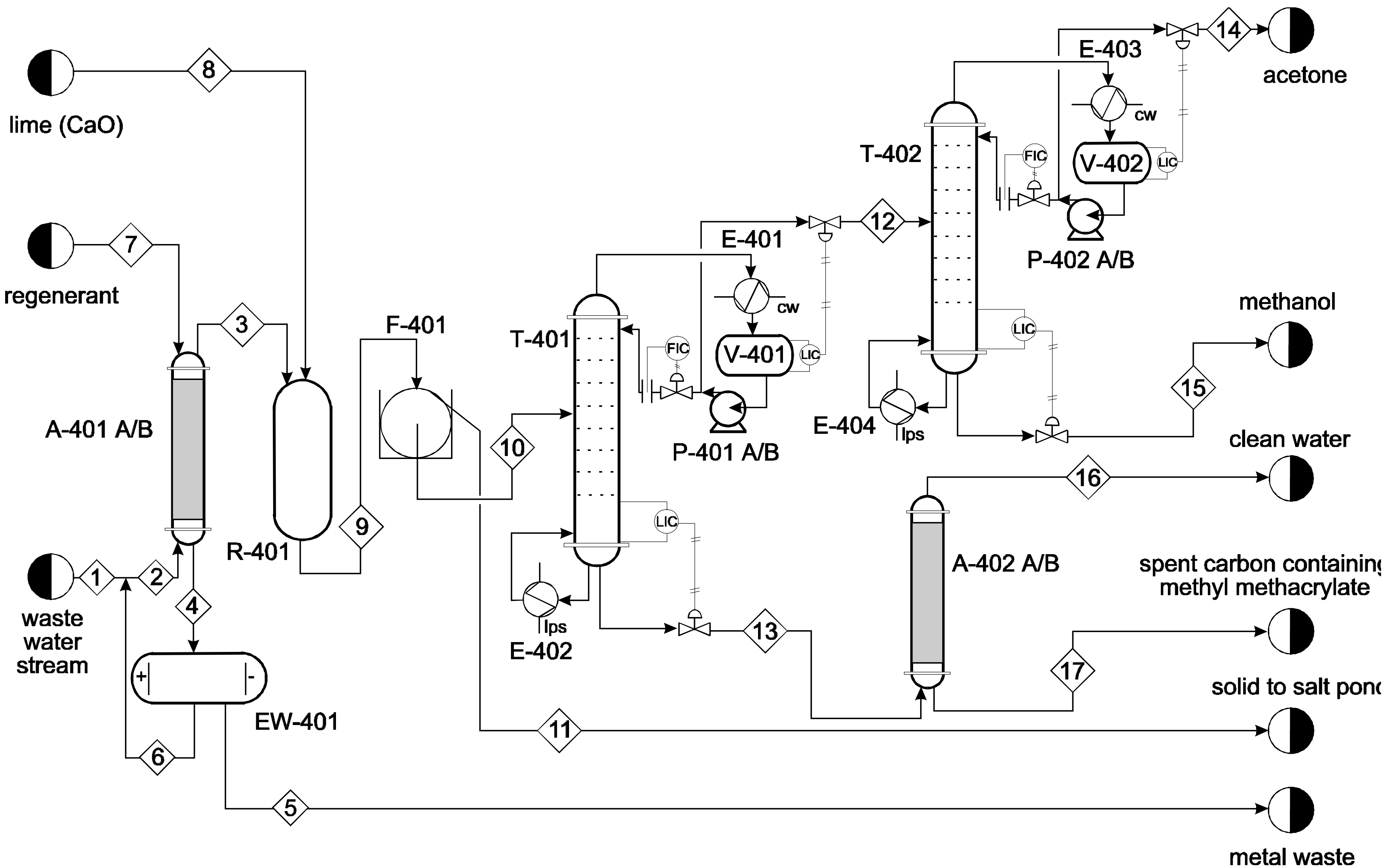
Stream No.	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**
Temperature (°C)	25.00	25.00	25.00	25.00	25.00	25.00	25.00	25.00	25.00
Pressure (kPa)	101.33	101.33	101.33	101.33	101.33	101.33	101.33	101.33	101.33
Vapor mole fraction	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Total Flow (kg/h)	2,369.83	*	2,369.28	**	0.38	**	***	1.33	2,370.60
Total Flow (mol/h)	131,415.61	*	131,410.51	**	5.10	**	***	23.65	131,410.51
Component Flowrates (mol/h)									
Water	131,329.46	--	131,329.46	--	--	--	***	--	131,353.11
Acetone	14.26	--	14.26	--	--	--	--	--	14.26
Methanol	14.76	--	14.76	--	--	--	--	--	14.76
Methyl Methacrylate	4.73	--	4.73	--	--	--	--	--	4.73
Hydrogen Fluoride	47.30	--	47.30	--	--	--	--	--	--
Lead (hydroxide)	0.23	--	--	--	--	--	--	--	--
Copper (hydroxide)	4.47	--	--	--	--	--	--	--	--
Tin (hydroxide)	0.40	--	--	--	--	--	--	--	--
Lead (nitrate)	--	--	--	0.23	--	--	--	--	--
Copper (nitrate)	--	--	--	4.47	--	--	--	--	--
Tin (nitrate)	--	--	--	0.40	--	--	--	--	--
Lead	--	--	--	--	0.23	--	--	--	--
Copper	--	--	--	--	4.47	--	--	--	--
Tin	--	--	--	--	0.40	--	--	--	--
Air	--	--	--	--	--	--	--	--	--
Calcium Oxide	--	--	--	--	--	--	--	23.65	--
Calcium Fluoride	--	--	--	--	--	--	--	--	23.65
Nitric Acid	--	--	--	--	--	--	***	--	--

* Stream 2 contains Streams 1 and 6 after mixing. We are not certain exactly what Stream 6 will consist of (explained in text) and are, therefore, unsure of Stream 2's composition as well. It is possible that Streams 1 and 2 will have the same composition.

** Streams 4 and 6 contain unknown amounts of water and nitrate which are required for the plating process. The flows of these streams are unknown at this time. If the electrowinning process is 100% efficient, the water will be pure in Stream 6.

*** The ion-exchange column capacity requires that 250 moles of nitric acid per cycle to regenerate the column; however, the required concentration and flowrate of the solution has not been determined. We believe a 1 M solution would most likely be suitable.

Stream No.	10	11	12	13	14	15	16	17
Temperature (°C)	25.00	25.00	25.00	25.00	25.00	25.00	25.00	25.00
Pressure (kPa)	101.33	101.33	101.33	101.33	101.33	101.33	101.33	101.33
Vapor mole fraction	0.00	0.00	0.00	0.00	0.00	0.00	0.00	solid
Total Flow (kg/h)	2,344.42	25.53	1.31	2,343.11	0.82	0.50	2,342.64	0.468
Total Flow (mol/h)	130,073.00	1,337.52	30.13	130,042.86	14.12	16.00	130,038.18	4.68
Component Flowrates (mol/h)								
Water	130,039.58	1,313.53	1.41	130,038.17	--	1.41	130,038.17	--
Acetone	14.11	0.14	14.12	--	13.97	0.14	--	--
Methanol	14.62	0.15	14.61	0.01	0.15	14.46	0.01	--
Methyl Methacrylate	4.68	0.05	--	4.68	--	--	--	4.68
Hydrogen Fluoride	--	--	--	--	--	--	--	--
Lead (hydroxide)	--	--	--	--	--	--	--	--
Copper (hydroxide)	--	--	--	--	--	--	--	--
Tin (hydroxide)	--	--	--	--	--	--	--	--
Lead (nitrate)	--	--	--	--	--	--	--	--
Copper (nitrate)	--	--	--	--	--	--	--	--
Tin (nitrate)	--	--	--	--	--	--	--	--
Lead	--	--	--	--	--	--	--	--
Copper	--	--	--	--	--	--	--	--
Tin	--	--	--	--	--	--	--	--
Air	--	--	--	--	--	--	--	--
Calcium Oxide	--	--	--	--	--	--	--	--
Calcium Fluoride	--	23.65	--	--	--	--	--	--
Nitric Acid	--	--	--	--	--	--	--	--



Treatment of a Waste Water Stream from Microelectronics Manufacture