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Production of Zinc Sulfide Pigment from Zinc-Containing Wastes

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This paper describes a new process for making zinc sulfide pigment from fiber industry waste. Technical-grade ZnO and high-quality ZnS were made in an environmentally clean manner, without any other waste product being produced. The equation and rate of ZnO dissolution (0.114 $L^{3/4} mol^{-3/4} min^{-1}$), as well as an empirical equation for determining the rate of ZnS precipitation, were found. Calculated and experimental data were in good agreement (<15%).

Introduction

Each year zinc-containing materials contribute about $40 billion to the global economy.[1,2] These products include metallic zinc, zinc alloys, household appliances, electronic components, pigments, dyes, fibers, rubbers, medications, fluorophores, specialty glasses, and plastics. Environmental regulations and the high cost, ~$1350 per ton, of metallic zinc in world markets necessitate the recovery of zinc.[3] The long life span of many zinc-containing products, such as brass fixtures, automobiles, and other galvanized coatings, represent a valuable and sustainable resource for future generations when zinc is recovered. Approximately 30% of the world's zinc supply, 2.9 million tons, comes from recycled zinc.[3,4]

Zinc can be recycled without loss of its physical and chemical properties. Many well-known pyrometallurgical and hydrometallurgical methods have been developed to recover zinc from waste materials. Most recently, Pelino described a hydrometallurgical process for converting zinc-containing industrial waste into glass and glass-ceramic materials,[5] and Sannina and co-workers developed a method for treating highly toxic solid waste obtained from electrolytic zinc based on self-propagating thermite reactions.[6] The purpose of this paper is to describe a general approach for recovering zinc from industrial fiber waste streams. The resulting product, technical-grade zinc oxide, can be reused as is or converted to zinc sulfide by H_2S precipitation.[7] The purity (99%) and particle size (~0.3 μm) of ZnS is of sufficient quality for use as a white pigment in plastics, printing inks, paints, coatings, reinforced fiberglass, lubricants, adhesives, putty, and insulating and sealing compounds. Other applications of zinc sulfide include color, semiconductor, luminescence, and phosphors.[8,9]

Experimental Section

Equipment and Materials. A temperature-controlled tube furnace, Lindberg/Blue M, from Thomas

Scientific (Swedeboro, NJ) was used in the calcination experiments. Potentiometric measurements were carried out at room temperature (25 ± 0.1 °C) in ammonium chloride buffers (0.5–2.0 M; 8.25 ≤ pH ≤ 10.25) using a Cole Parmer (Vernon Hills, IL) model KW-59003-30 instrument. Saturated Ag/AgCl reference and zinc amalgamated indicator electrodes were used. In the zinc dissolution experiments, the indicator electrode consisted of zinc oxide with 3% starch paste pressed into a 25-mm-diameter Teflon disk. The exposed surface, 3 mm in diameter, was dried, polished, and rotated at 600 rpm (Pine Instruments, Grove City, PA).

The potentiometric measurements were confirmed by titration with sodium ethylenediaminetetraacetic acid (EDTA) with eriochrome black T as the indicator. All reagents were purchased from Fisher Scientific (Pittsburgh, PA) and used as received. Technical-grade zinc oxide was obtained from EMPILS Corp. (Rostov-on-Don, Russia).

The physical and chemical composition of fibrous waste is dependent on the plant capacity and the type of fibers made, as well as the pretreatment, transportation, and storage practices. In this study, waste material was taken from 22 fiber plants from the former Soviet Union. Generally, the total zinc content in the waste ranged from 6 to 41% by mass. Table 1 lists the highest and lowest concentrations of zinc in the waste. The metal content is reported as the metal oxide found in the waste. Also shown is the total carbon, carbonate carbon, total sulfur, sulfate sulfur, and percent volatiles produced at 1000 °C. The sample studied was fortified to represent the statistical mean of each component found in the 22 plants and consisted of finely dispersed particles, approximately 15% in concentration.

Results and Discussion

Figure 1 depicts the block diagram of zinc recycled from artificial fiber industry wastes. The technological process includes the following main stages: (1) filtration and drying of the waste (slime) material, (2) calcination of the desiccated slime to obtain technical-grade zinc oxide and coating tiles as coproducts, (3) dissolution of zinc oxide in ammonium chloride buffer solution, (4)

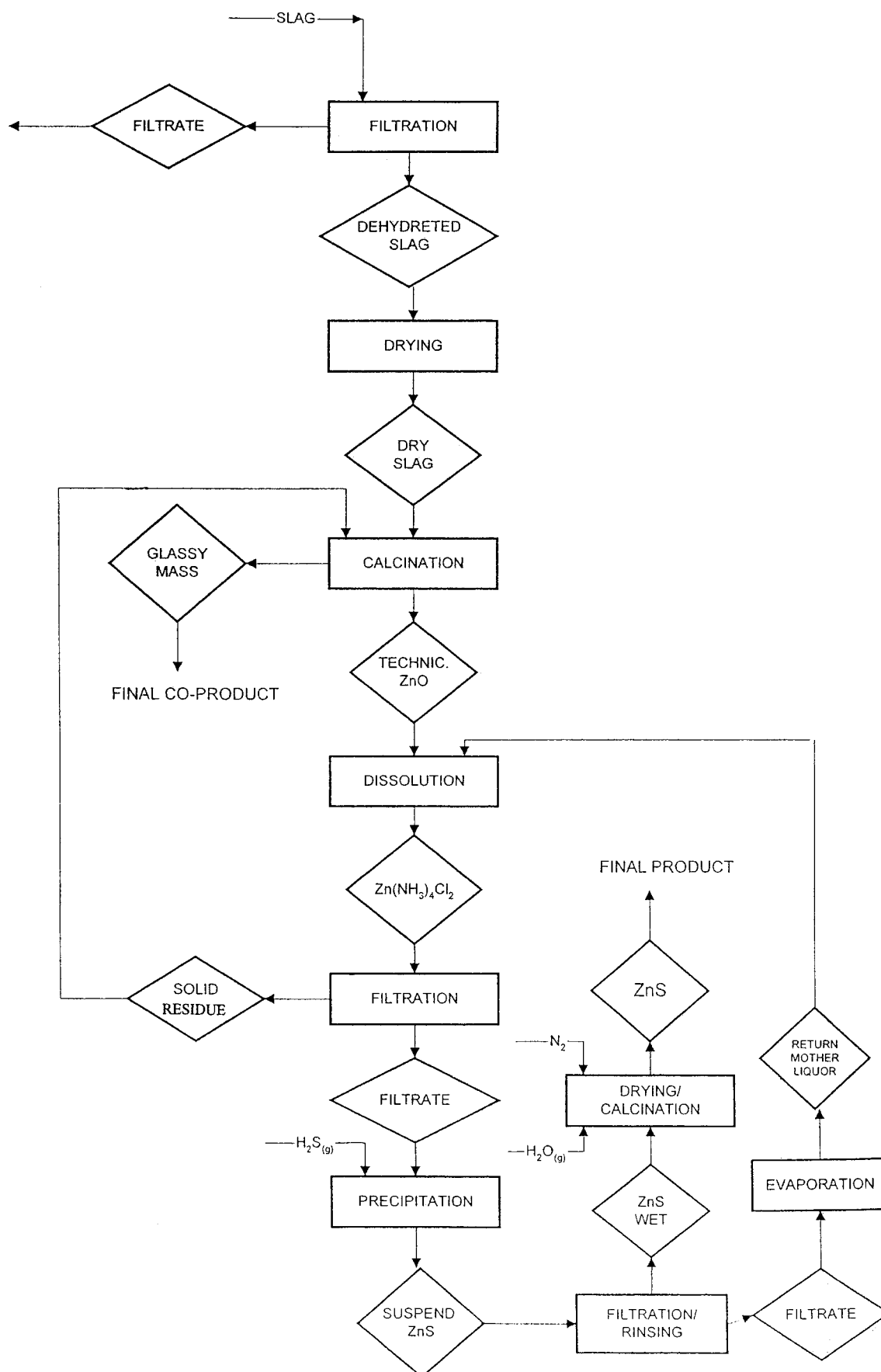* Corresponding author: Albert Robbat. E-mail: arobbat@tufts.edu. Phone: 617-627-3474.

Figure 1. Technological block schematic of zinc-containing waste treatment process.

precipitation of zinc sulfide, (5) separation of the liquid and solid phases and adjustment of the filtrate volume
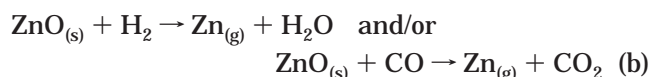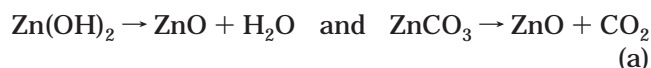
and buffer composition for reuse in the dissolution stage, and (6) drying and calcination of the raw zinc sulfide

Table 1. Chemical Composition (% mass) of the Highest, Lowest, and Statistical Mean Disperse Phase of Zinc-Containing Fiber Industry Wastes (Russia)

plant	ZnO	Al_2O_3	Fe_2O_3	CaO	MgO	SiO_2	C_{total}	C_{carb}	S_{total}	$S_{sulfate}$	Na_2O	K_2O	volatile
Svetlogorsk	74.5	0.6	1.3	1.6	0.1	1.5	12.5	7.0	3.5	1.9	2.2	0.1	1.6
Kamensk	6.2	4.6	2.6	19.4	2.9	24.5	16.9	14.1	5.4	3.7	0.3	0.2	17.0
statistical mean	19.2	2.7	2.9	15.8	1.1	19.3	15.2	9.6	5.2	4.8	2.0	0.3	15.7

into white pigment. As can be seen, the only waste is the filtrate from step 1, which is returned to the plant's initial waste stream system. Consequently, all solid waste streams can be recycled, making this process environmentally clean.

Dry Slime Calcination. The solid waste was calcinated in a two-chamber cyclone furnace.[10] The air-to-methane ratio was adjusted to maintain the temperature in the furnace between 1250 and 1300 °C. Zinc oxide was produced from the waste by reaction a. In the presence of reducing agents, zinc is converted into gaseous zinc (see reaction b) and then transported into chamber 2.

$$Zn(OH)_2 \rightarrow ZnO + H_2O \quad \text{and} \quad ZnCO_3 \rightarrow ZnO + CO_2 \quad \text{(a)}$$

$$ZnO_{(s)} + H_2 \rightarrow Zn_{(g)} + H_2O \quad \text{and/or}$$
$$ZnO_{(s)} + CO \rightarrow Zn_{(g)} + CO_2 \quad \text{(b)}$$

At this temperature, all other components remain in chamber 1 as a liquid forming a glassy mass that can be converted to coating tiles upon cooling. The atmosphere in chamber 2 was made oxidative by adding air above the stoichiometric ratio (see reaction c). Technical-grade zinc oxide (mp 1975 °C) was collected using the dust extractor system and can be used as a final product or made into zinc sulfide pigment

$$2Zn_{(g)} + O_2 \rightarrow 2ZnO_{(s)} \quad \text{(c)}$$
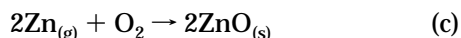
Dissolution of Zinc Oxide. ZnO was dissolved in an equimolar ammonium chloride buffer solution

$$ZnO_{(s)} + 2NH_4OH_{(aq)} + 2NH_4Cl_{(aq)} \rightarrow$$
$$[Zn(NH_3)_4]Cl_{2(aq)} + 3H_2O \quad \text{(d)}$$
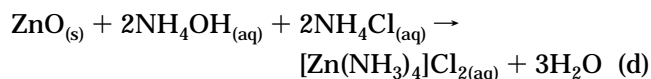
The instability constant of the tetra-ligand complex is 3.46×10^{-10}, with dissolution proceeding practically to completion (at pH = 9.25, 99.2% tetraligand). The rate of dissolution was monitored by potentiometry and found using a rotated disk[11] with zinc oxide impregnated
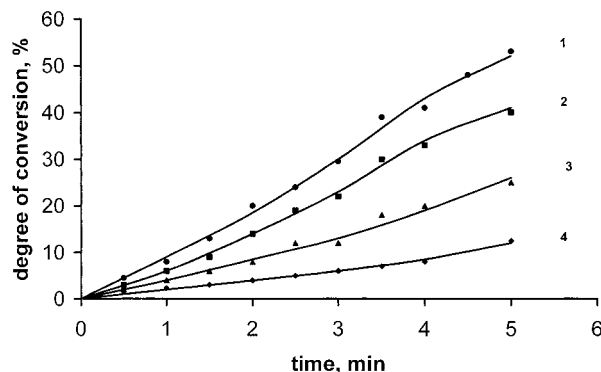
into the working surface of the electrode.[12] The zinc ion concentration was measured as a function of time, where ΔE is the change in the zinc-amalgamated electrode potential. Figure 2 shows the percent conversion of ZnO to $[Zn(NH_3)_4]Cl_2$ at fixed and varying concentrations of NH_4Cl and NH_4OH, respectively. Conversely, Figure 3 shows data where the concentration of NH_4OH is fixed and that of NH_4Cl changes. We found the NH_4OH and NH_4Cl reaction orders to be 1 and $3/4$, respectively; that is

$$w = k[NH_4OH][NH_4Cl]^{3/4} \quad \text{(1)}$$

where k is the rate constant of the reaction. The amphiprotic nature of NH_4^+ in water might account for the fractional kinetic order in NH_4Cl. This might be due to the fact that NH_4^+ hydrolyzes in water, making ammonium hydroxide. The rate of dissolution of ZnO is higher in solutions containing only NH_4OH as opposed to those containing only NH_4Cl, and it is highest when both species are present in solution. Equation 1 can be rewritten in dimensionless coordinates, taking into account the reaction stoichiometry from eq d, to find k

$$dx/d\tau = 3.364kC_0^{3/4}(a - x)(b - x)^{3/4} \quad \text{(2)}$$

The constant is derived from the reaction stoichiometry. $x = C_\tau/C_0$, is the degree of ZnO conversion into the tetramminzinc(II) complex; C_τ is the concentration of the complex at time τ; C_0 is the maximum concentration of the complex that can be obtained from the ZnO disk electrode; $a = C_1^0/2C_0$ and $b = C_2^0/2C_0$; and C_1^0 and C_2^0 are the initial concentrations of NH_4OH and NH_4Cl in the buffer, respectively. Equation 2 can be integrated to give

$$k = [1/(3.364C_0^{3/4}\tau)]\int_0^x dx/(a - x)(b - x)^{3/4} \quad \text{(3)}$$

which can be solved analytically when $a = b$ (or when the initial concentrations of the components in solution
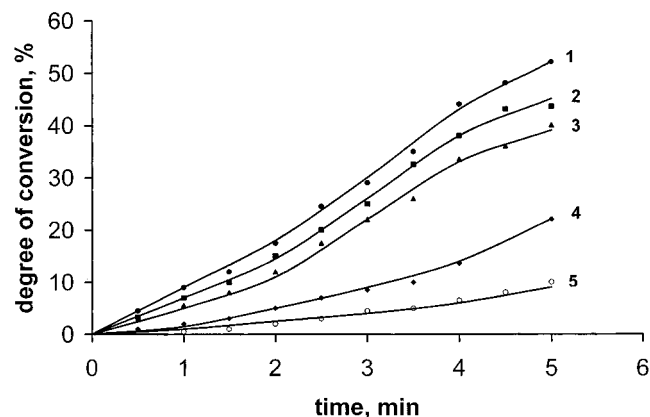
Figure 2. Kinetics of zinc oxide dissolution as a function of ammonium hydroxide concentration at 25 °C: C_{NH_4Cl} = 2 mol/L; C_{NH_4OH} (mol/L) for curve 1, 2.0; for curve 2, 1.5; for curve 3, 1.0; for curve 4, 0.5.

Figure 3. Kinetics of zinc oxide dissolution as a function of an ammonium chloride concentration at 25 °C: C_{NH_4OH} = 2 mol/L; C_{NH_4Cl} (mol/L) for curve 1, 5.0; for curve 2, 3.0; for curve 3, 2.0; for curve 4, 1.0; for curve 5, 0.5.

are equal), yielding

$$k = 0.397[a^{3/4} - (a - x)^{3/4}]/[\tau C_0^{3/4}(a - x)^{3/4}] \quad (4)$$

The average value of k is 0.114 ± 0.010 $L^{3/4}$ $mol^{-3/4}$ min^{-1} at 25 °C when $C_1^0 = C_2^0 = 2$ mol/L, $C_0 = 0.058$ mol/L, and $n = 600$ rpm.[13] The activation energy for this reaction is 40.5 kJ/mol (linear regression statistics: $y = -0.451x + 15.463$; $r^2 = 0.992$), confirming that the process is kinetically controlled at the specified disk rotation rate.

Zinc Sulfide Precipitation. Zinc precipitation from the tetramminzinc(II) complex was performed with gaseous hydrogen sulfide. As shown in reaction e, the products after precipitation have the same solution composition as in the ZnO dissolution process.

$$[Zn(NH_3)_4]Cl_{2(aq)} + H_2S_{(g)} + 2H_2O \rightarrow$$
$$ZnS_{(s)} + 2NH_4OH_{(aq)} + 2NH_4Cl_{(aq)} \quad (e)$$
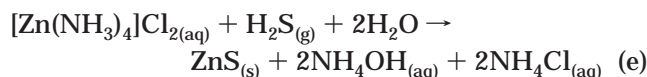
The only difference is the amount of water (3 mol) formed during dissolution compared to the number of moles needed for precipitation. The excess water is evaporated, and the remaining liquid recycled. Because gaseous H_2S is fed into solution, which also contains a surplus of ammonium chloride buffer (at least 5-fold), precipitation proceeds via the conence-ion mechanism at a very high reaction rate

$$Zn(NH_3)_4^{2+}{}_{(aq)} + S^{2-}{}_{(aq)} \rightarrow ZnS_{(s)} + 4NH_{3(aq)} \quad (f)$$
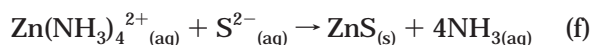
where eq f is the sum of several stepwise reactions [conence $Zn^{\phi}(NH_3)_{4-n}$, where $1 \leq n \leq 4$ and the symbol ø indicate unsaturated bonds in this complex].

Because the ion interaction is fast, the whole process can be limited by mass transfer (external diffusion) at the gas/liquid interface. The zinc sulfide precipitation kinetics for different values of hydrogen sulfide partial pressure in the transmitting phase are given in Figure 4. Examination of the data shows that the precipitation rate is proportional to the volume velocity, which is the transmitting gas (hydrogen sulfide) volume passed per unit time through the reactor solution volume ([Zn-$(NH_3)_4]Cl_{2(aq)}$). Therefore, precipitation increases with increasing hydrogen sulfide volume velocity (Figure 5). If the number of moles of H_2S is divided by the number of moles of zinc ions in solution, then all experimental points obtained for different zinc ion concentrations fall on a single line (Figure 6). The degree of conversion x at 25 °C can be calculated by the following equation, where $n^0_{Zn^{2+}}$ is the initial number of moles of zinc in solution and n_{H_2S} is the number of moles of hydrogen sulfide introduced into solution at time τ.

$$x = 1.48\tau^{3/4} n_{H_2S}/n^0_{Zn^{2+}} \quad (5)$$

Equation 5 describes the curve in Figure 6. Table 2 shows a comparison between the calculated (obtained using eq 5) and experimentally derived values of x at different hydrogen sulfide concentrations (partial pressures). Except for the results at $n_{H_2S} = 0.024$ ($p_{H_2S} = 0.1$ atm), the relative percent differences (RPDs) were less than 20%, with most data within $\pm 5\%$. The diffusion kinetics for ZnS precipitation can be obtained from the data in Figures 4 and 6 and is described by eq 6, where R is the universal gas constant, T is the absolute
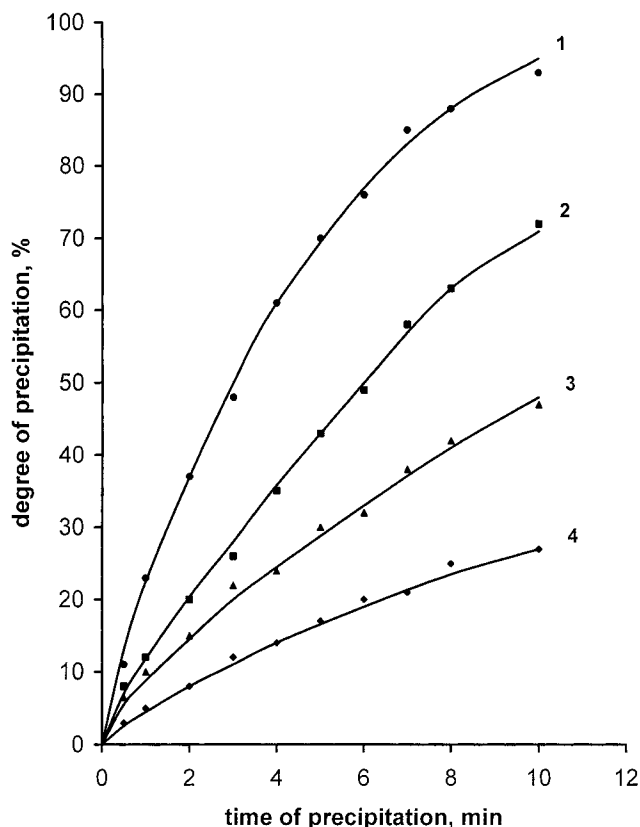
Figure 4. Kinetics of zinc sulfide precipitation at 25 °C: $C_{Zn^{2+}} = 1.0$ mol/L; $V_{gas} = 5.33$ L/min; p_{H_2S} (atm) for curve 1, 0.6; for curve 2, 0.4; for curve 3, 0.3; for curve 4, 0.1.

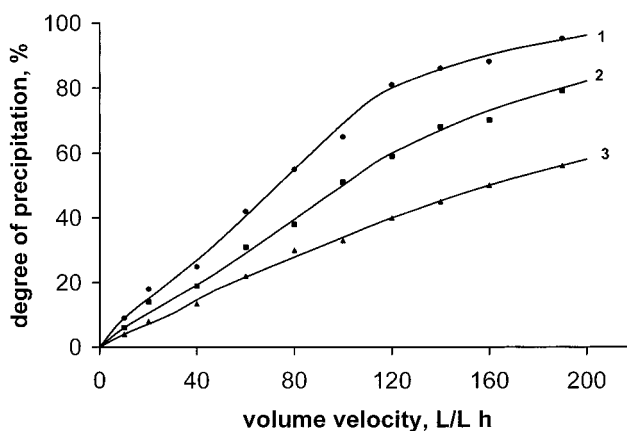**Figure 5.** Influence of the volume velocity on the rate of zinc sulfide precipitation at 22 °C: $C_{Zn^{2+}} = 2.0$ mol/L; time (min) of precipitation for curve 1, 9 min; for curve 2, 6 min; for curve 3, 4 min.

temperature, and K is the experimental constant w_{exp}/w_{calc}.

$$w = KRT(1 - x)(n_{H_2S})^{2/3}/\tau^{1/4} n^0_{Zn^{2+}} \quad (6)$$

The values of K at four different partial pressures of H_2S are shown in Table 3. The average K value was $0.060 \pm 13\%$. By seeding the solution with ZnS crystals and providing rapid mixing, the process can be optimized. Once the solid is separated from the liquid, zinc sulfide can be turned into a pigment through the application of heat.

Calcination of the Raw Zinc Sulfide. The covering power of ZnS pigment is dependent on the size and

Table 2. Comparison of Experimental and Calculated Degrees of ZnS Precipitation (x)

t (min)	$t^{0.75}$	$n_{H_2S} = 0.13$			$n_{H_2S} = 0.087$			$n_{H_2S} = 0.065$			$n_{H_2S} = 0.024$		
		x_{calc}	x_{exp}	RPD	x_{calc}	x_{exp}	RPD	x_{calc}	x_{exp}	RPD	x_{calc}	x_{exp}	RPD
0.5	0.6	11	11	0	8	8	0	6	6	0	2	3	35
1	1	19	22	13	13	12	−7	10	9	−7	4	5	34
2	1.68	32	36	11	22	20	−8	16	14	−14	6	8	29
3	2.28	44	47	7	29	28	−5	22	20	−9	8	11	30
4	2.83	54	60	10	36	36	−1	27	23	−17	10	12	18
5	3.34	64	70	9	43	41	−5	32	30	−7	12	16	30
6	3.83	74	76	3	49	50	1	37	34	−8	14	18	28
7	4.3	83	83	0	55	56	1	41	38	−8	15	21	32
8	4.76	92	88	−4	61	62	1	46	43	−6	17	23	31
10	5.62	108	93	−15	72	69	−5	54	48	−12	20	26	26

Table 3. Determination of the ZnS Precipitation Constant $K = w_{exp}/w_{calc}$[a]

τ, min	$\tau^{0.25}$	x	$(1 - x)$	w_{calc}	w_{exp}	K	x	$(1 - x)$	w_{calc}	w_{exp}	K
			$n_{H_2S} = 0.13$ mol						$n_{H_2S} = 0.087$ mol		
0.5	0.84	0.11	0.89	6.592	0.410	0.062	0.08	0.92	5.211	0.290	0.056
1	1.00	0.20	0.8	4.978	0.350	0.070	0.17	0.83	3.949	0.210	0.053
2	1.19	0.36	0.64	3.346	0.230	0.069	0.22	0.78	3.119	0.170	0.055
3	1.32	0.45	0.55	2.593	0.178	0.069	0.29	0.71	2.559	0.148	0.058
4	1.41	0.59	0.41	1.809	0.130	0.072	0.36	0.64	2.16	0.128	0.059
5	1.50	0.65	0.35	1.452	0.105	0.072	0.42	0.58	1.84	0.109	0.059
6	1.57	0.72	0.28	1.110	0.079	0.071	0.50	0.50	1.515	0.100	0.066
7	1.63	0.81	0.19	0.725	0.053	0.073	0.56	0.44	1.284	0.091	0.071
8	1.68	0.86	0.14	0.519	0.037	0.071	0.62	0.38	1.076	0.072	0.067
10	1.78	0.91	0.09	0.315	0.021	0.067	0.67	0.33	0.882	0.068	0.077
			$n_{H_2S} = 0.065$ mol						$n_{H_2S} = 0.024$ mol		
0.5	0.84	0.06	0.94	4.369	0.230	0.053	0.04	0.96	2.29	0.140	0.061
1	1.00	0.12	0.88	3.436	0.178	0.052	0.08	0.92	1.84	0.099	0.054
2	1.19	0.19	0.81	2.657	0.137	0.052	0.10	0.9	1.51	0.081	0.054
3	1.32	0.22	0.78	2.307	0.120	0.052	0.13	0.87	1.32	0.075	0.057
4	1.41	0.27	0.73	2.021	0.105	0.052	0.15	0.85	1.21	0.069	0.057
5	1.50	0.30	0.70	1.822	0.093	0.051	0.18	0.82	1.09	0.061	0.056
6	1.57	0.34	0.66	1.641	0.088	0.054	0.20	0.8	1.02	0.059	0.058
7	1.63	0.39	0.61	1.461	0.082	0.056	0.25	0.75	0.92	0.053	0.058
8	1.68	0.43	0.57	1.325	0.075	0.057	0.27	0.73	0.87	0.050	0.058
10	1.78	0.49	0.51	1.119	0.065	0.058	0.29	0.71	0.80	0.046	0.058

[a] $T = 298$ K, $C_{Zn^{2+}} = 1$ mol/L.
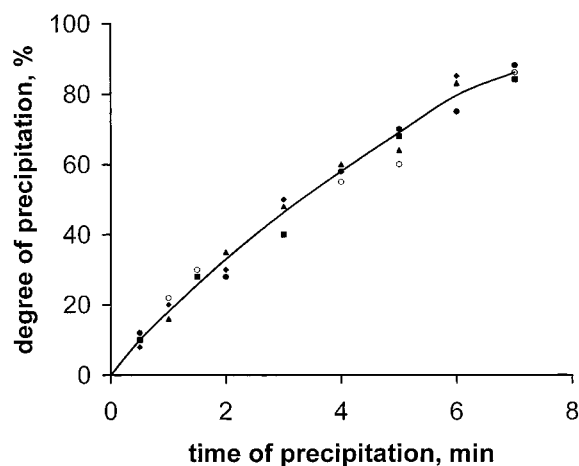
Figure 6. Diffusion kinetics of zinc sulfide precipitation in adjusted coordinates at 25 °C: $V_0 = 6.7$ L/(min mol); $p_{H_2S} = 0.4$ atm; $C_{Zn^{2+}}$ (mol/L) ○, 0.10; △, 0.25; ■, 0.70; ●, 0.80; ◆, 1.0.

shape of the particles. Calcination of ZnS was carried out in an inert atmosphere (N$_2$, CO, CO$_2$, H$_2$O) at 650 °C for 25 min. If 20−25% steam is introduced into the oven, then the final product will exhibit the best pigment characteristics. Although the mechanism is unclear, it can be hypothesized that hydroxyl bridges are formed on the particle surface as a result of the interaction between ZnS and H$_2$O$_{(g)}$. These bridges appear to help the colloidally dispersed particles to coagulate into 0.2−0.5 μm aggregates of pigment.

Conclusion

A new process for making high-quality zinc sulfide pigment from zinc-containing waste was described. First, the waste was converted to technical-grade zinc oxide. Then, ZnO was made into zinc sulfide pigment. The kinetic equation for ZnO dissolution was found over a wide temperature range with varying concentration of buffer. H$_2$S was used to precipitate ZnS. The equation for estimating the rate of precipitation was also found, with the rate dependent on the gas volume velocity. Calculated and experimental results were in good statistical agreement (<15%), suggesting that this environmentally clean system might provide a good economic means for making ZnO and ZnS.

Nomenclature

a, b = initial adjusted concentrations of NH$_4$OH and NH$_4$Cl, respectively

C_1^0, C_2^0 = initial concentrations of NH$_4$OH and NH$_4$Cl, respectively, mol/L

C_0 = maximum concentration of [Zn(NH$_3$)4]Cl$_2$ in solution, mol/L

C_τ = current concentration of complex in solution, mol/L

$[i]$ = concentration of ith compound in solution, mol/L

k = rate constant, L$^{3/4}$ mol$^{-3/4}$ min^{-1}

n = number of revolutions of the rotation disk, rpm

n_i = number of moles of ith compound

$n^0_{Zn^{2+}}$ = initial number of moles of zinc ions in solution

p_{H_2S} = partial pressure of hydrogen sulfide, atm

R = universal gas constant, J mol^{-1} K^{-1}

t = temperature, °C
T = absolute temperature, K
V_o = volume velocity, L/(L min)
w = rate of appropriate chemical reaction, mol/min or min^{-1}
x = degree of conversion, %
τ = time, min

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