Environment Protection Engineering

Vol. 1 1975 No. 2

JANUSZ BARCICKI*, JERZY NIEĆKO*, LUCJAN PAWŁOWSKI*

INVESTIGATIONS OF ALUMINIUM PRECIPITATION FROM ALKALINE WASTE-WATER

The paper is concerned with waster-water resulting from surface treatment of aluminium wares. The results of the waste-water neutralization combined with aluminium precipitation with CO_2 and combustion gases are presented. Final pH value of the waste-water as well as the effect of temperature on the precipitate settleability and degree of aluminium removal from the waste-water have been determined.

1. INTRODUCTION

Surface treatment of aluminium sheets, containers, and other products with solution of natrium hydroxide is associated with strong alkalinity of the resulting waste-water. Its alkalinity increases, moreover, due to large amounts of aluminium hydroxide suspensions as the effect of hydrolysis of aluminates present in the waste-water. The both factors are harmful for water environment and should be carefully controlled. For this reason the investigations on neutralization of the waste-water and on precipitation of aluminium in form of aluminium hydroxide were performed on the request of a big factory. The average contents of aluminium (in form of aluminates) and natrium hydroxide in one liter of waste-water amounted to 3.7 g and 24 g, respectively.

Neutralization of the above waste-water with mineral acids, pure CO_2 and waste gases has been taken into account. Mineral acids result in high water content precipitate of aluminium hydroxide; consequently, the clarification degree is very low, amounting to about 10%. Much better results can be obtained by using either pure CO_2 or combustion gases containing carbon dioxide.

Diagram 1 illustrates the solution pH as the concentration function of various forms of carbonic acid. It may be seen that within the pH range required for the

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*J. Barcicki, J. Niećko, L. Pawłowski, Maria Skłodowska-Curie University, Institute of Chemistry, Lublin, ul. Nowotki 8, Poland.

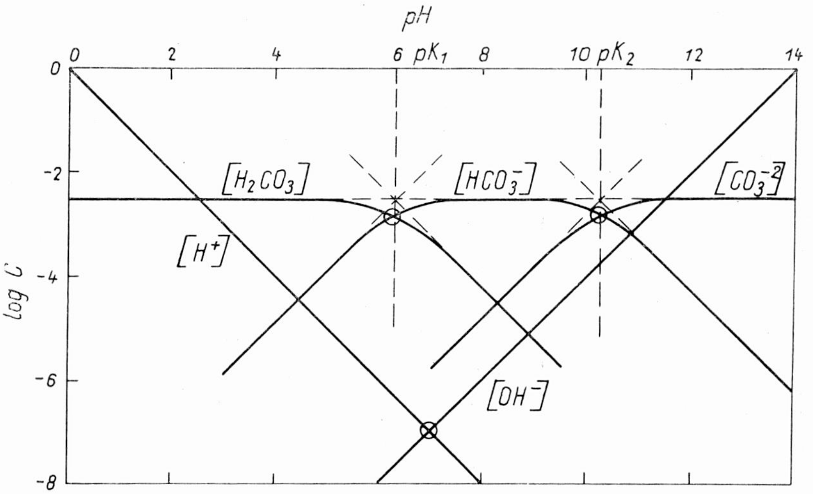

Fig. 1. pH vs. H^+, CO_3^{-2}, HCO_3^- and CO_2 concentrations [2]

Rys. 1. Diagram ilustrujący zależności pomiędzy pH oraz stężeniami H^+, CO_3^{-2}, HCO_3^- i CO_2 [2]

neutralized waste-water acid sodium carbonate prevails. This means that neutralization of one gram-equivalent of the base requires one mol of CO_2. The structure of the resulting precipitate, and hence the degree of waste-water clarification, depends on CO_2 content in saturation gas and on the temperature of waste-water. In view of the above mineral acids were excluded as the neutralizing agents. Hence the effects of carbonization method by means of pure CO_2 and combustion gases as well as the influence of waste-water temperature and its final pH on suspension settleability and on residual aluminium content in clarified waste-water have been determined.

2. EXPERIMENTALS

2.1. NEUTRALIZATION IN A BATCH SYSTEM

Schematic representation of the experimental apparatus used for waste-water carbonization is given in Fig. 2. The waste-water neutralized to a given pH value was transferred to cylinders, where the resulting precipitate settleability was determined. After an 8 hour sedimentation the volume of precipitate was measured and the residual aluminium content in supernatant determined by titrating with EDTA in presence of PAN indicator, according to Polish standards [4]. The percent of aluminium in the precipitate has been, moreover, determined. The results obtained for carbonization by means of pure CO_2 are given in Table 1 for combustion gases being presented in Tables 2 and 3. Waste gases contained about 10% of CO_2.

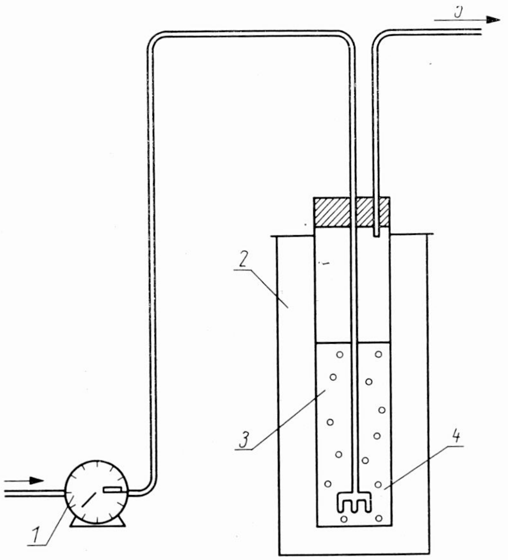

Fig. 2. Schematic representation of the laboratory batch saturation unit
1 — CO_2 or waste gas supply, *2* — thermostate, *3* — saturator, *4* — gas diffusers, *5* — vacuum outle

Rys. 2. Schemat instalacji laboratoryjnej do przeprowadzania saturacji w układzie periodycznym
1 — doprowadzanie CO_2 lub gazów spalinowych, *2* — termostat, *3* — saturator, *4* — barbotki, *5* — wyjście do próżni.

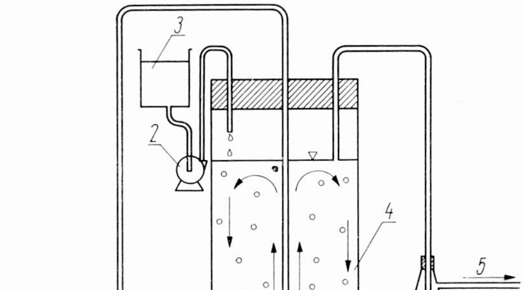

Fig. 3. Schematic representation of laboratory unit used to saturation in a continuous flow system
1 — CO_2 or waste gas supply, *2* — waste dosing pump, *3* — waste container, *4* — saturator, *5* — vacuum outlet, *6* — waste collector (test samples)

Rys. 3. Schemat instalacji laboratoryjnej do przeprowadzania saturacji w układzie ciągłym
1 — doprowadzanie CO_2 lub gazów spalinowych, *2* — pompa dozująca ścieki, *3* — zbiornik ścieków, *4* — saturator, *5* — wyjście do próżni, *6* — kolektor ścieków (próbki do analizy)

Table 1

Waste neutralization with pure CO_2

Zestawienie parametrów neutralizacji ścieków czystym dwutlenkiem węgla

Temperature K	After saturation pH	$\frac{h}{H}\cdot 100\%$	$\frac{h_1}{h}\cdot 100\%$	Aluminium in deposit after sedimentation %	Aluminium content in clarified waste after 8 hr sedimentation mg/dm^3
296.2	7.68	30.7	100	1.20	2.43
	8.53	36.4	100	1.02	3.95
	9.30	46.6	53.9	0.79	17.7
	9.80	61.6	36.2	0.60	58.1
311.4	8.00	24.0	100	1.54	1.26
	9.05	35.7	69.3	0.99	10.5
	9.69	49.3	40.0	0.75	31.1
321.9	8.02	18.5	100	2.00	1.26
	8.25	20.6	100	1.80	1.72
	9.24	42.2	57.2	0.88	12.2
329.0	8.00	12.0	100	3.08	2.38
	8.22	12.9	100	2.87	4.55
	8.70	13.8	100	2.68	4.55
	9 12	32.9	83.5	1.12	12.6
336.8	8.10	12.3	100	3.01	3.43
	8.25	12.4	100	2.98	3.40
	8.60	13.5	100	2.74	4.20
	9.63	55.0	38.7	0.67	27.4
342.6	8.35	8.57	100	4.33	2.32
	9.05	17.6	75.0	2.10	8.71
	9.35	33.3	55.2	1.11	25.1
348.5	8.35	7.14	100	5.18	3.53
	8.52	7.43	100	4.97	4.13
	9.38	31.0	53	1.19	14.3
	9.88	61.7	45	0.60	73.7
351.8	8.50	7.73	100	4.78	3.39
	9.35	25.0	75.0	1.48	12.4
	9.92	82.3	23.5	0.45	196
369.4	8.72	5.06	100	7.31	4.30

2.2. NEUTRALIZATION IN A CONTINUOUS-FLOW SYSTEM

Neutralization in a continuous-flow system has been performed using laboratory apparatus shown in Fig. 3.

It appeared, that in the installation of this type water content in the precipitate was very high; its properties were comparable with those of sediment precipitated by mineral acids; consequently the clarification percent was rather low.

3. DISCUSSION

In generally two zones have been observed in the settled suspensions: supernatant zone *A* and voluminous precipitate zone — *B*. In some cases an additional interface has been distinguished within zone *B* giving fluffy deposite zone *B* and compact deposite zone *C*. (see Fig.4). The settling properties of the precipitates resulting from neutralization of waste-water have been compared by determining the percentage by volume of the phases *B* or $B+C$ after an 8 hr undisturbed sedimentation. The thickening of the sludge was characterized by voluminous percentage of the compact sludge with respect to its total volume, $(C/B+C)\cdot 100$. The corresponding values are given in Tables 2 and 3.

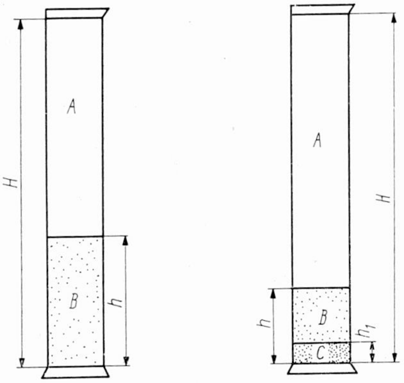

Fig. 4. Course of sedimentation

A — clarified waste-water, *B* — homogeneous deposit, *C* — dense deposit

Rys. 4. Ilustracja przebiegu sedymentacji.

A — sklarowane ścieki, *B* — osad jednolity, *C* — osad gęsty

The effects of temperature and of final pH value on precipitate settleability and sludge thickening as well as on the degree of aluminium removal have been also examined.

Table 2

Waste neutralization with combustion gases

Zestawienie parametrów z neutralizacji ścieków gazami spalinowymi

Temperature K	pH after saturation	$\frac{h}{H}\cdot 100\%$	$\frac{h_1}{h}\cdot 100\%$	% aluminium in deposit after sedimentation	Aluminium content in clarified waste after 8 hr sedimentation mg/dm^3	$\frac{\text{V comb. gases}}{\text{V waste}}$	$\frac{\text{V comb. gases}}{\text{V waste}\cdot t}$ h^{-1}
294.2	10.60	76.1	0.00	0.49	1310	124	188
	10.45	67.8	8.93	0.55	730	216	183
	10.10	58.6	15.6	0.63	212	312	186
	9.37	39.4	32.2	0.94	12.2	468	171
	9.05	19.6	75.0	1.89	10	648	174
	8.70	11.8	100	3.14	4.90	860	174
	8.64	10.5	100	3.52	3.23	892	175
	8.59	9.13	100	4.05	3.15	960	170
298.2	10.38	65.1	9.65	0.57	645	248	182
	9.40	38.2	22.0	0.97	16	552	187
	9.11	20.2	68.3	1.83	10.8	692	180
	8.80	13.8	100	2.68	6.67	920	173
	8.85	13.5	100	2.74	3.31	1084	175
	8.48	12	100	3.08	2.03	1184	174
305.0	10.28	78.3	17.5	0.47	429	284	180
	9.88	58.7	22	0.63	60.7	424	177
	8.91	14.8	100	2.50	6.06	908	173
	8.66	13.1	100	2.82	4.01	1100	162
	8.49	13	100	2.85	2.13	1276	142
323.2	10.40	69.8	5	0.53	638	276	167
	9.37	57.4	38.6	0.64	16.2	700	157
	9.12	22.5	75	1.64	11.1	856	144
	8.95	12.3	100	3.01	5.9	960	130
	8.67	11	100	3.36	3.88	1200	122
344.6	10.17	54.3	10.6	0.68	294	372	150
	9.80	47.2	20	0.78	45.4	528	136
	9.21	31.8	54.3	1.16	37.4	888	127
	9.02	16.2	87.3	2.28	8.78	996	109
	8.85	9.32	100	3.97	4.91	1140	102
355.3	10.25	52.4	5	0.71	365	368	134
	9.7	46.2	21	0.8	48	684	119
	9.25	32.1	63.1	1.15	15.7	1016	110
	9.03	14	90	2.64	10.2	1128	97.3
	8.82	9.17	100	4.03	4.6	1428	84.5

Table 3

Time dependence of sedimentation*

Charakterystyka przebiegu sedymentacji w czasie

Sedimentation time, h	0	$\frac{1}{6}$	$\frac{1}{2}$	1	2	5	8	24	48
Percent of deposit	100	80.0	55.0	43.2	24.9	16.3	12.0	9.08	8.80
Aluminium content in clarifed waste (phase *A*), mg/dm^3	3700	1470	483	103	25.0	10.4	2.03	1.90	1.85
pH	8.48	8.51	8.56	8.64	8.70	8.81	8.89	9.98	9.01

* Waste saturated with combution gases at 298 K to pH = 8.48.

From the data presented in Tables 2 and 3 it follows that the sludge volume is proportional to the pH value.

Percent of aluminium in the sludge is closely related to sludge volume and this, in turn, depends on final pH at the end of waste-water saturation with CO_2. The same refers to aluminium concentration in supernatant.

For pH < 9 the aluminium content was smaller than 9 ppm. Starting with pH value equal to 9 its content increases rapidely. A high aluminium content is not admissible, since dilution of waste-water occurring at its discharge to receiving water body results in hydrolysis, and this process yields in large amount of suspension. Other important parameters in neutralization of waste-water with waste gases are: gas/waste-water volumetric ratio and flow rate of these gases through the saturator. The laboratory tests have shown that the value of waste-water pH falls below 9 at ambient temperature for the ratio 800: 1. At higher temperatures this ratio rises up to 1200: 1. The decrease in flow-rate observed in our experiments was caused by the clogging of the gas diffusers. This phenomenon was particularly distinct at higher temperatures, since the precipitate is more easily deposited on the walls and submerged elements. It should be also mentioned that the deposite obtained at higher temperatures compared with that formed at lower temperature is less soluble in alkali and acids. This is of importance since the precipitate of aluminium hydroxide obtained in this way can be utilized, e.g. to produce coagulants. To this end aluminium should be introduced to the solution.

The data given in Table 3 characterize time dependence of sedimentation process. A fast increase in the clarification percent and decrease in Al conc. in upper layer of clarified liquid have been stated. The value of pH is variable, slightly increasing with sedimentation time. This increase was observed in all cases, being more pronounced for suspensions obtained at lower pH values.

BADANIA NAD WYTRĄCANIEM GLINU Z ALKALICZNYCH ŚCIEKÓW

W artykule przedstawiono wyniki badań nad neutralizacją połączoną z wytrącaniem glinu za pomocą dwutlenku węgla i gazów spalinowych ze ścieków powstających przy trawieniu wyrobów aluminiowych. Określono wpływ pH, do jakiego doprowadzono ścieki, i temperatury na zdolność sedymentacyjną zawiesin i stopień wytrącania glinu ze ścieków.

VERSUCHE ZUR AUSFÄLLUNG VON ALUMINIUM AUS ALKALISCHEN ABWÄSSERN

In Beitrag werden die Versuche zur Al-Ausfällung und zur Neutralisation von alkalischen Aluminiumbeizen eingehend erörtert. Beide Forderungen erfüllt die Begasung der Abwässer mit Kohlendioxyd und Verbrennungsgasen. Diskutiert wird der Einfluß des pH-Wertes und der Temperatur auf die Absetzfähigheit der Schwebestoffe sowie auf die Fällungsrate des Aluminiums aus dem Abwasser.

ИССЛЕДОВАНИЯ ПО ОСАЖДЕНИЮ АЛЮМИНИЯ ИЗ ЩЕЛОЧНЫХ СТОЧНЫХ ВОД

Представлены результаты исследований по нейтрализации, сопровождаемой осаждением алюминия при помощи двуокиси углерода и выхлопных газов из сточных вод, образующихся при травлении изделий из алюминия. Определено влияние pH, до какого были приведены сточные воды, а также температуры на седиментационную способность суспензий и осаждаемость алюминия из загрязненной воды.

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