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A NOVEL PROCESS FOR THE NEUTRALIZATION OF NaOH AT AN ALUMINIUM SEMIMANUFACTURES PRODUCTION FACILITY

NOV NEVTRALIZACIJSKI POSTOPEK NaOH PRI PROIZVODNJI ALUMINIJEVIH POLIZDELKOV

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During the production of aluminium semifactures on presses there are some tools that must be cleaned because they are covered with aluminium. The tools are soaked in a 20% solution of sodium hydroxide (NaOH) in which the aluminium is dissolved. The tools are then washed with water, which causes a problem because it contains 30-50 mg Al per 1000 ml.There is also a problem with the waste hydroxide, which contains 200 g of NaOH per 1000 ml and 120 g Al per 1000 ml.

To avoid environmental polution and the high costs of NaOH regeneration a new way of hydroxide neutralization has been found. The proces is based on the neutralization of NaOH with carbon dioxide (CO_2) in the reaction vessel. During this reaction $NaHCO_3$ is formed and the Al is adsorbed onto an added adsorbent. At the bottom of reaction vessel this mix is filtered. The filtered water is clean and can be allowed to flow into the sewage system. The residue is dried and because it is no longer toxic it can be used.

Before starting the process of neutralization in production some laboratory tests had to be made first. The chemical composition and the concentrations of input and output substances were determined as well as chemical reactions during the process of neutralization. Determination of the concentrations of input and output substances was made by inductively coupled plasma atomic absorption spectrometry (ICP-AES).

Keywords: aluminium, neutralization, sodium, waste sodium hydroxide, inductively coupled plasma atomic emission spectrometry

Pri proizvodnji aluminijevih polizdelkov na stiskalnici je treba očistiti orodja, ki prihajajo v stik z aluminijem. Čiščenje poteka z namakanjem orodij v 20-odstotni raztopini natrijevega hidroksida (NaOH), v kateri se aluminij raztopi. Orodja nato sperejo z vodo. Pri čiščenju nastajajo težave zaradi odpadnega luga, ki vsebuje 200 g NaOH / 1000 ml in 120 g Al / 1000 ml, ter odplak, ki vsebujejo 30-50 mg Al / 1000 ml.

Da bi se izognili visokim stroškom regeneracije NaOH in onesnaževanju okolja so pripravili nov način nevtralizacije luga. Postopek temelji na nevtralizaciji luga z ogljikovim dioksidom (CO_2) v reakcijski posodi, kjer nastane natrijev hidrogen karbonat ($NaHCO_3$), aluminij pa se adsorbira na dodanem adsorpcijskem sredstvu. Na dnu reakcijske posode se ta mešanica filtrira. Prečiščena voda je neoporečna in lahko odteče v kanalizacijo. Suhi preostanek se dodatno osuši in ker je okolju prijazen, se lahko uporablja za posipanje cest, v gradbeništvu, itd.

Za vpeljavo te vrste nevtralizacije je bilo treba najprej izvesti laboratorijski preizkus ter spoznati kemijsko sestavo in koncentracije vhodnih surovin, kemijske reakcije, ki potekajo med nevtralizacijo in kemijsko sestavo, ter koncentracije izhodnih surovin. Za določevanje koncentracij vhodnih in izhodnih surovin smo uporabili atomsko emisijsko spektrometrijo z induktivno sklopljeno plazmo (ICP-AES).

Ključne besede: aluminij, nevtralizacija, natrij, odpadni natrijev hidroksid, atomska emisijska spektrometrija z induktivno sklopljeno plazmo

1 INTRODUCTION

Over the last few decades aluminium's ecological and biological effects have been under discussion. It is well known that this metal is harmful to several organisms, such as fish[1,2], algae[3] and plants[4]. Aluminium has been shown to be toxic to humans as well, especially for renal insufficiency patients undergoing dialysis[5]. During the 1970s it was discovered that long-term exposure to aluminium from the water supply used with dialysis equipment causes a progressively fatal neurological condition called dialysis dementia[6]. This condition is now clearly linked to an increased level of Al in the body, specifically the bioaccumulation of aluminium in the brain, bone and other tissues[6]. There is also the possibility that aluminium may be an aetiological factor in Alzheimer's Disease, which is another reason for the increased interest in the biological significance of aluminium[7-12]. However, the biological activity of aluminium depends on the forms in which the metal occurs[13]. In order to get a better measure of aluminium's toxicity considerable efforts have been put into developing analytical techniques for fractionating aluminium in natural waters[14-17]. Most of the methods measure "labile forms" of aluminium, i.e. the sum of Al^{3+} and aluminium's monomeric complexes with hydroxide, sulphate and often fluorides. These forms of aluminium are believed to be the more toxic to e.g. fish than aluminium's complexes with e.g. citrate or organic ligands[13].

There are two major problems that make it difficult to determine aluminium at trace levels: lack of sensitivity and difficulty in sample handling due to contamination[5]. Sensitive methods such as atomic absorption spectrometry with electrothermal atomization (ETA-AAS) suffer from serious matrix interferences and contamination prloblems[18]. Alternatives such as inductively coupled plasma atomic emission spectrometry (ICP-AES) and flame atomic absorption spectrometry (FAAS) with higher limits of detection need preconcentration of the analyte[19,20]. Online preconcentration techniques have also been applied to FAAS[21,22], but the detection limit is not low enough to determine aluminium in dialysis samples. Fluorimetric methods are very sensitive and the instrumentation is readily available, but they usually lack selectivity[23]. Inductively coupled plasma mass spectrometry (ICP-MS) has recently been proposed for the deteremination of aluminium in dialysis samples[24] due to its very low detection limit (1 ng ml^{-1}), but it suffers from a susceptibility to matrix effects and a standard addition method must be used for each sample.

Aluminium is easily determined at higher than trace levels because dilution can be applied and thus matrix effects are reduced. For this reason ICP-AES is a suitable technique for Al determination. The high temperature of the atomization/ionization plasma of ICP-AES suits refractory elements such as aluminium and also quickly destroys the matrix, thus minimizing the analytical interferences. The continuous integrated signal also gives superior precision when compared with ETA-AAS[25].

For these reasons ICP-AES has been found to be the most convenient technique for aluminium and sodium determination in waste sodium hydroxid (NaOH) and water from aluminium semifactures products on presses. NaOH is used for cleaning the tools, which are then washed with water. Both the hydroxide and the water are contaminated with aluminium and they must be regenerated before flowing into the sewage system. A new method of hydroxide neutralization is reported in this article. Its advantage is that after neutralization of the NaOH with carbon dioxide (CO_2) soluble $NaHCO_3$ is obtained and the Al is adsorbed onto the added adsorbent. This mix is then filtered. The water is no longer toxic and can flow into the sewage system. The residue is then dried and can be used, for exapmple, as a building material, on the roads in winter, etc.

2 EXPERIMENTAL

2.1 Instrumentation

All analyses were carried out with the Perkin Elmer OPTIMA 3100RL simultaneous ICP-AES instrument (Perkin Elmer, Überlingen, D). The instrument operating parameters used are shown in **Table 1**. Readings of the pH were made with the Iskra MA 5705 pH meter and the HEC 0101 combined electrode. The home-made reactor for hydroxide neutralization was a combination of a CO_2 flask, a valve for CO_2 flow measurement, a polyethylene tube and a flask for introducing gas to the sample.

Table 1: Instrument parameters and operating conditions for ICP-AES
Tabela 1: Instrumentalni parametri in delovne razmere za ICP-AES

Spectrometer	PERKIN ELMER, simultanious, radial, model OPTIMA 3100 RL
Polichromator	Echelle
Detector	SCD
Resolution	0.006 nm at 200 nm
Spectral range	165 – 403 nm
RF generator	
Frequency	40 mhz, free-running
Power output	1300 w
Output power stability	< 0.1 %
ICP source	
Plasma torch	Quarz with 2.0 mm al_2o_3 injector
Plasma argon flow	15 l min^{-1}
Auxilary argon flow	0.5 l min^{-1}
Nebulizer argon flow	0.8 l min^{-1}
Observation height	15 mm above load coil
Sample introduction area	
Spray chamber	Scott-type, Ryton
Nebulizer	Gemtype cross-flow, pneumatic
Peristaltic pump	1 ml min^{-1}
Analytical parameters	
Flush time	30 s
Integration time	5 - 10 s

2.2 Solutions

A stock solution of Al was prepared by dissolving 1 g ± 0.0005 g of pure Al (99.99%) in HCl (1+1). A few drops of HNO_3 (1.40 g ml^{-1}) were added and the nitric fumes were expelled. The solution was cooled and transfered to a 1000-ml flask.

A stock solution of Na was prepared by dissolving 1.7291 g ± 0.0005 g of NaOH in distilled water. After cooling the solution was transfered to a 1000-ml flask.

A synthetic solution with similar concentrations of Al and Na to those found in waste hydroxide was prepared by dissolving NaOH in distilled water and pure Al in HCl (1+1). Both solutions were combined, cooled and transfered into a 1000-ml flask.

2.3 Calibration

Calibration sets were prepared by diluting the stock solutions with distilled water in the range of 5-25 mg l^{-1} for Al and 8-40 mg l^{-1} for Na.

3 RESULTS AND DISCUSSION

For successful neutralization the input concentrations of Al and Na in the waste hydroxide and the waste water, as well as the pH of both solutions had to be determined. After suitable dilution with distilled water and the addition of 2 ml of HCl (1.18 gm l^{-1}) to 100 ml, Al and Na were determined by ICP-AES. To select the optimum spectral line for each element, sample preparation, matrix effects, spectral interferences and the sensitivity of the spectral lines were taken into account. The spectral interferences for Al and Na are summarized in **Table 2**. The values presented were determined by sampling a 1000 mg l^{-1} solution of a potentially interfering element and determining the apparent concentration at each wavelength. After considering all the obtained data we selected the 394.401 nm Al line and the 330.237 nm Na line.

Table 2: Spectral interferences (apparent concentrations in mg l^{-1})
Tabela 2: Spektralne interference (navidezna koncentracija v mg l^{-1})

Element	Line	Interfering element (1000 mg l^{-1})	
		Na	Al
Na	330.237	-	0,05
Na	330.298	-	0,15
Na	288.114	-	8,54
Al	394.401	- 0,14	-
Al	308.215	- 0,26	-
Al	237.313	- 0,15	-

The concentrations of Al and Na obtained from the original samples are shown in **Table 3**. They were slightly different from the data supplied by the factory because the characteristics of waste hydroxide and water probably change with aging. The pH of the original waste hydroxide was >14 and the pH of the waste water was 7.

Table 3: Concentrations of Al and Na in original samples
Tabela 3: Koncentracije Al in Na v originalnih vzorcih

	data from factory		determined	
	w. hydroxide	w. water	w. hydroxide	w. water
Al	12 %	30-50 mg l^{-1}	up to 15 %	up to 25 mg l^{-1}
NaOH	20 %	n.d.	up to 38 %	-
Na	11.6 %	n.d.	22 %	17 mg l^{-1}

First the sodium hydroxide was diluted 1+1 with distilled water, but this did not work because the tube from the CO_2 flask was immediately clogged: the next dilution was 1+10. To determine the best gas flow we tried with CO_2 flows of 4, 6 and 8 l min^{-1}. For all flow rates the precipitate was formed after 10 minutes of bubbling through. At a gas flow of 4 l min^{-1} the pH of the solution remained 8 no matter how long the bubbling through took. At a gas flow of 8 l min^{-1} the clogging occured again. We decided to choose a gas flow of 6 l min^{-1}.

To achieve complete neutralization, we varied the time of bubbling through at a constant gas flow of 6 l min^{-1} and at a constant dillution of 1+10. We found that the pH of the solution became neutral only after the solution was filtered and after a second bubbling through the filtrate for 15 minutes. At the second bubbling through the precipitate did not occur any more. More concentrated solutions require a longer time for the first bubbling through to reach pH 7. The dependence of pH on the time of bubbling through is shown in **Figure 1**. The first three columns represent the dilution 1+10 and the second three the dilution 1+5.

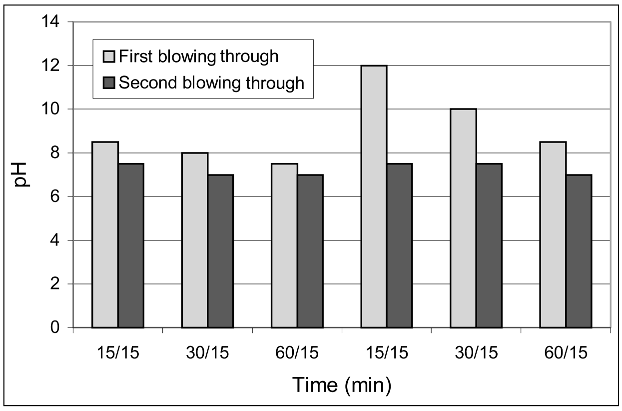

Figure 1: Depenedence of pH on the time of gas flow at 6 ml min^{-1}
Slika 1: Odvisnost pH od časa prepihovanja pri pretoku plina 6 ml min^{-1}

We found that for the laboratory neutralization test the most convenient gas flow is 6 l min^{-1}. For lower gas flows the neutralization could not be achieved and for higher gas flows the clogging was a problem.

The process of neutralization was as follows: 20 ml of waste hydroxide was diluted to 200 ml with distilled water and CO_2 was bubbled through at a flow of 6 l min^{-1} over a period of 15-60 minutes. The solution was filtered with the help of a water pump. The precipitate was dried at 105 °C for 2 hours, dissolved in 100 ml of HCl (1.18 g ml^{-1}) and diluted to 500 ml with distilled water. Again, CO_2 was bubbled through the filtrate for 15 minutes, 100 ml of HCl (1.18 g ml^{-1}) was added to the filtrate and transferred to a 500-ml flask. Prior to Al and Na determination the solutions were further diluted with distilled water as shown in **Table 4** to eliminate matrix effects.

Table 4: Dilution of samples by determination of Al and Na
Tabela 4: Razredčitve vzorcev za določevanje Al in Na

Determination	Dilution	
	Filtrates (F)	Precipitations (P)
Al	20ml/500ml-10ml/50ml	20ml/500ml-10ml/100ml-1ml/50ml
Na	20ml/500ml-10ml/50ml-1ml/100ml	20ml/500ml-10ml/100ml-10ml/100ml

Because of the lack of certified reference materials a synthetic solution with similar concentrations of Al and Na to those found in the waste hydroxide was prepared to control the accuracy of the results. The synthetic solution was subjected to the same procedure of

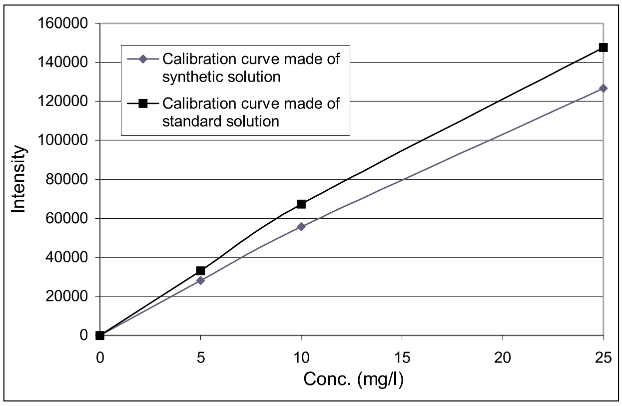

Figure 2: Calibration curves for Al
Slika 2: Umeritveni krivulji za Al

neutralization as the samples of waste hydroxide and waste water. As the input concentrations of Al and Na in the waste water were too low, no changes occured after bubbling the CO_2 through.

To determine Al and Na concentrations calibration curves derived from standard solutions of Al and Na were drawn. By comparing the results of the synthetic solution with the real values we found that the concentrations were too low. Next we prepared new calibration curves using suitable dilutions of the synthetic solution so the matrix was the same as in the samples. The differences between the two calibration curves are shown in **Figures 2 and 3**.

The results were accurate this time as is shown in **Table 5**. The dilution prior to neutralization for samples 1-5 was 1+10, for samples 6-8 it was 1+5 and sample 9 was a synthetic solution diluted 1+5. The dilution prior to ICP-AES determination were as shown in **Table 4**.

Table 5: Results of Al and Na determination
Tabela 5: Rezultati določevanja Al in Na

Sample	μg Al	% Al	μg Na	% Na
1F	0,59	0,0074	16,67	20,84
2F	0,63	0,0079	15,55	19,44
3F	0,34	0,0043	15,56	19,45
4F	0,62	0,0078	15,90	19,88
5F	0,30	0,0038	15,82	19,78
6F	0,26	0,0033	14,45	18,06
7F	0,36	0,0045	14,85	18,56
8F	0,10	0,0013	11,96	14,95
9F	0,17	0,0022	10,99	13,74
1P	10,28	12,85	14,86	3,72
2P	10,00	12,50	18,61	4,65
3P	10,26	12,83	18,62	4,66
4P	9,82	12,28	14,88	3,72
5P	10,10	12,63	17,05	4,26
6P	10,34	12,93	24,25	6,06
7P	10,40	13,00	23,93	5,98
8P	10,39	12,99	38,81	9,70
9P	8,53	10,66	13,23	3,31
waste w.	1,25	0,00025	6,54	0,0013

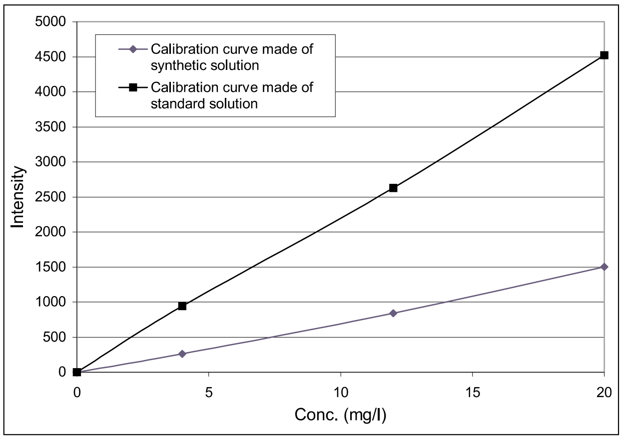

Figure 3: Calibration curves for Na
Slika 3: Umeritveni krivulji za Na

Instead of diluting the samples with distilled water prior to neutralization, the waste water from the process was be used because of its low concentrations of Al and Na.

The results were as satisfactory as the previous ones and they are shown in **Table 6**.

Table 6: Results of Al and Na determination (dilution with waste water)
Tabela 6: Rezultati določevanja Al in Na (razredčitev z odplako)

Sample	μg Al	% Al	μg Na	% Na
waste w.	1.25	0.00025	7.86	0.0016
waste hydr.	8.34	13.34	17.26	27.62
10 F	0.18	0.0018	31.97	20.39
11 F	0.40	0.005	27.46	20.35
10 P	13.07	13.07	20.39	6.39
11 P	10.73	13.41	16.28	6.87

4 CONCLUSIONS

In this study the laboratory neutralization of waste hydroxide from the production of aluminium semimanufactures on presses was investigated. We found that after bubblingcarbon dioxide through the solution with a gas flow of 6 l min^{-1} after 15-60 minutes the precipitate formed and after a second bubbling through the filtrate became neutral. The products, water soluble $NaHCO_3$ and $Al(OH)_3$, adsorbed onto the added adsorbent, are no longer harmful to the environment because they are in non-toxic forms.

When the reactor and the neutralization proces are used in production the amounts of waste hydroxide and water, as well as the gas flow, will be larger. The clogging due to gas cooling on expansion will probably not be a problem any more because of the broader tubes and the speed of the neutralization. All these parameters will be examined on site.

5 REFERENCES

[1] J. R. Kramer, J. Hummel, and J. Gleed, in J. N. Lester, R. Perry and R. M. Sterritt (EDS), *Proc. Int. Conf. Chem. Environ.*, Selper, London, 1986, 636-641

[2] J. D. Birchall, C. Exley, J. S. Chappell and M. J. Phillips, *Nature* (London), 1989, 338, 146

[3] S. Helliwell, G. E. Batley, T. M. Florence and B. G. Lumsden, *Inviron. Technol. Lett.*, 4 (**1983**) 141

[4] M. Andersson, *Water Air Soil Pollut.*, 39 (**1988**) 439

[5] A. Martin-Esteban, P. Fernandez, C. Perez-Conde, A. Gutierrez and C. Camara, *Anal. Chim. Acta*, 304 (**1995**) 121

[6] A. C. Alfrey, G. R. LeGendre and W. D. Kaehny, *N. Engl. J. Med.*, 294 (**1976**) 184

[7] D. R. Crapper, S. S. Krishnan and S. Quittkat, *Brain*, 99 (**1976**) 67

[8] D. P. Perl, W. W. Pendlebury and D. Munoz-Garcia, *in Proceedings of the First International symposium on Geochemistry and Health*, ed. I. Thornton, Science Reviews, Northwood, UK, 1985, 227

[9] D. R. McLahlan, *Neurobiol. Aging*, 7 (**1986**) 525

[10] R. Katzman, *N. Engl. J. Med.*, 314 (**1986**) 964

[11] D. R. McLahlan, W. J. Lukiw and T. P. Kruck, *Can. J. Neurol. Sci.*, 16 (**1989**) 490

[12] G. L. Eichhorn, *Exp. Gerontol.*, 28 (**1993**) 493

[13] C. T. Driscoll, J. P. Baker, J. J. Bisogni and C. L. Schofield, *Nature* (London), 184 (**1980**) 161

[14] R. Barnes, *Chem. Geol.*, 15 (**1975**) 177

[15] C. T. Driscoll, *Int. J. Environ. Anal. Chem.*, 16 (**1984**) 267

[16] P. M. Bertsch and M. A. Anderson, *Anal. Chem.*, 61 (**1989**) 535

[17] S. Schmid, W. Kördel, H. Klöppel and W. Klein, *J. Chromatogr.*, 470 (**1989**) 289

[18] A. D. Woolfson and Gracey, *Analyst*, 112 (**1987**) 1387

[19] M. R. Pereiro, A. Lopez, M. E. Diaz and A. Sanz mendel, *J. Anal. At. Spectrom.*, 5 (**1990**) 15

[20] S. Hirata, K. Honda and T. Kumamru, *Anal. Chim. Acta*, 221 (**1992**) 65

[21] H. J. Salacinki, P. G. Riby and S. J. Haswell, *Anal. Chim. Acta*, 269 (**1992**) 1

[22] B. Mohammad, A. M. Ure and D. Littlejohn, *J. Anal. At. spectrom.*, 7 (**1992**) 695

[23] F. Hernandez Hernandez and J. Medina Escriche, *Analyst*, 109 (**1984**) 1585

[24] P. L. Trentini, M. Ascanelli, B. Zanforlini, F. Venturini, G.Buchi and F. Fagioli, *J. Anal. At. Spectrom.*, 8 (**1993**) 905

[25] T. J. Burden, J. J. Powell, R. P. Thompson and P. D. Taylor, *J. Anal. At. Spectrom.*, 10 (**1995**) 259