

Effects of Alkaline Aluminate Waste Dumping on Seawater Chemistry

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ABSTRACT

The alkaline aluminate waste, of which 1000–2000 tonnes are dumped a few times a year off the Belgian coast in the Southern Bight of the North Sea, contains 5.4% NaCl, 1.8% dissolved Al and 7.4% NaOH, in addition to traces of heavy metals and some aniline- and phenol-derivatives. The pH rises locally to 8.5 and the total Al-concentration reaches $120 \text{ mg litre}^{-1}$ (corresponding to an initial waste dilution factor of only 150) in the 10-m wide track just beyond the discharging barge, but these decay quickly to pH 8.1 and 1 mg litre^{-1} in the 30-m wide track, 500 m behind the barge. The relation between the waste concentration and seawater pH was studied. The white precipitate that forms immediately in the sea was identified as $\text{Mg}_6\text{Al}_2\text{CO}_3(\text{OH})_{16} \cdot 4\text{H}_2\text{O}$ (hydrotalcite-manasseite like). No trace of it was found in the local sediments.

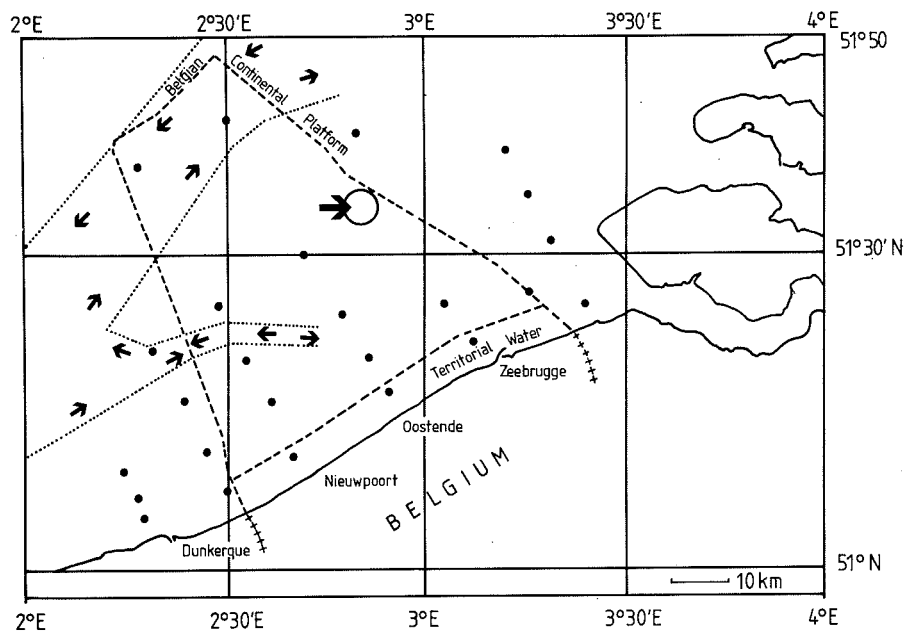
INTRODUCTION

In the alkylation of anilines for the production of various types of herbicides and fungicides, aluminium catalysts are often used. After reaction, this catalyst is destroyed by adding water, which leads to important volumes of solutions containing typically 7% NaOH, 5% NaCl and 6% NaAlO_2 , with minor concentrations of organic and inorganic pollutants. The total amount, produced in Belgium, to be dumped into the North Sea, is in the order of $5000 \text{ tonnes yr}^{-1}$.

The possible adverse effects of this dumping on the marine environmental quality are rather controversial. The biotoxicity and the geochemical



(a)



(b)

Fig. 1. (a) Map of the North Sea with dumping area indicated. (b) Detail, with the theoretical dumping site and shipping routes.

behaviour of aluminium in the marine environment are still under research. Whereas a detailed study of Baeteman (1986) showed an LC_{50} level (96 h) around 6 g litre^{-1} of waste or $100 \text{ mg litre}^{-1}$ of Al for the shrimp *Crangon crangon* and plaice *Pleuronectes platessa*, Bergtsson (1978) reported an LC_{50} (96 h) Al dose of 10 mg litre^{-1} for the copepod *Nitocra spinipes* and Petrich & Reish (1979) reported an LC_{50} (96 h) level for *Ctenodrilus* of $0.48 \text{ mg litre}^{-1}$ (as AlCl_3). The latter authors concluded that Al has a similar biotoxicity to polychaetes as cadmium and chromium.

Much has also been published lately on the geochemical behaviour of Al in seawater. Although it is a major component of the Earth's crust, its concentration in unpolluted seawater is extremely low: below $1 \mu\text{g litre}^{-1}$ in oceanic water and up to $10 \mu\text{g litre}^{-1}$ in coastal water (Caschetto & Wollast, 1979; Hydes, 1979). Many controlling reaction pathways including both inorganic and biochemical processes (Stoffijn & Mackenzie, 1982) have been invoked in order to explain such low levels.

It seemed, therefore, important to investigate the dilution characteristics and the behaviour of Al during such massive aluminate waste dumping. During such an operation between 1000 and 2000 tonnes of waste are pumped into the Southern Bight of the North Sea, some 30 km off the Belgian coast (see Fig. 1a and b). The barge circles at a maximum speed of 25 km h^{-1} around the site $51^{\circ}35'\text{N}$, $2^{\circ}50'\text{E}$ with a 4 km diameter, and discharges the waste into its wake at a maximum rate of $720 \text{ m}^3 \text{ h}^{-1}$. The dumping area is characterised by a depth of 25 m and a relatively strong current (around 3 cm s^{-1} from the English Channel to the NNE).

MATERIALS AND METHODS

Analysis procedures

The waste samples were analysed as follows. The base content was determined by HCl titration after addition of NaF. The amount of chloride was assessed by titration with AgNO_3 after neutralisation of the waste with H_2SO_4 . The concentration of aluminate was measured using zinc-acetate, after addition of HCl, EDTA and a back-titration using ammonia. The other inorganic pollutants were assessed via atomic absorption spectrometry, differential-pulse anodic stripping voltametry and DCP-emission spectrometry, after acidification of the sample with HCl, or via spark source mass spectrometric analyses on a 2-ml dried sample mixed with graphite (Vandelannoote *et al.*, 1981). In combination with photoplate detection, the latter technique is truly panoramic and shows typical detection limits of 50 ppb (atomic). The organic composition was assessed in

two ways: phenols were extracted in acid medium with dichloromethane, while anilines were extracted in alkaline medium. Analysis was done using gas chromatography-mass spectrometry, taking into account the relative sensitivity factors for the individual components.

The observed white solid phase was analysed using energy-dispersive X-ray fluorescence, electron microprobe analysis with a JEOL 733 Superprobe equipped with both wavelength- and energy-dispersive X-ray spectrometry attachment, X-ray diffraction, infrared spectroscopy, differential thermal analysis and laser microprobe mass analysis with the LAMMA-500 instrument. The principles and possibilities of the latter novel technique have been discussed by Denoyer *et al.* (1982).

Field sampling and analysis

Two different approaches were used:

A first survey was carried out on 4 May 1984, using the small MSI *Kortrijk* vessel, quite similar to that described by Roekens & Van Grieken (1983). Reference samples (seawater and sediment) were taken outside the dumping area. Thirty-five seawater samples were taken during the dumping operation using 5-litre Nansen sampling bottles in order to establish the vertical and horizontal dilution patterns of the waste. The pH was measured on the spot using a glass electrode. Small aliquots of water were filtered through 0.4 μm pore-size Nuclepore membrane filters and acidified. The Al content of the eluate was measured in the laboratory using a fluorimetric lumogallion method (Hydes & Liss, 1976); the linearity, reliability and blank levels of those determinations were thoroughly checked previously (Van Grieken & Vandelannoote, 1985). Four sediment samples were also collected 1 km downstream from the dumping site. Low wind velocities and a calm sea occurred during this sampling.

The second survey was carried out on 17 November 1984 from the Belgian research vessel *Belgica*. The horizontal distribution of the waste cloud was investigated by sampling from a small Zodiac inflatable, which allows sampling as close as 30 m from the dumping ship. Thirty samples were taken at 1 m depth in the centre of the waste track up to 600 m behind the barge. To assess perpendicular surface profiles, the Zodiac crossed the track perpendicularly to the moving direction of the barge; 10 and 19 samples were then taken at about 200 and 500 m, respectively, behind the barge. No filtration or acidification was done in the field. The pH was measured in the laboratory. The total amount of Al (dissolved and suspended) was assessed, after acidification (in order to dissolve all Al present) and suitable dilution. No reliable depth profiling could be done at sea because of the strong winds (5–6 Beaufort).

RESULTS

Composition of the alkaline aluminate waste

The average composition of alkaline aluminate waste from a plant in Belgium is given in Table 1. The results corresponded very well with the producer's analytical report. The concentration limits set in the dumping permission are not exceeded, except for Cu (by a factor of 2). A typical dumping event in which about 1000 tonnes of waste is discharged, implies the following input to the marine environment: 65 tonnes NaOH, 45 tonnes NaAlO_2 or 15 tonnes Al, 45 tonnes NaCl, 210 g Cr, 900 g Cu, 1300 g Zn, 25 g Cd, 350 g Pb, 180 kg phenol-derivatives and 35 kg aniline-derivatives.

Profiles of pH and aluminium before alkaline aluminate dumping

The reference samples taken just outside the dumping area showed an average pH of 8.07 and an average 'dissolved' Al content of 6.6, 7.1 and $10.1 \mu\text{g litre}^{-1}$, at depths of 3, 15 and 25 m, respectively. The pH value is similar to that of 7.94–8.10 reported by Roekens & Van Grieken (1983).

TABLE 1
Average Composition of the Alkaline Aluminate Waste

<i>Parameter</i>	<i>Measured concentration</i>
Specific density	1.18 g cm^{-3}
Dry residue	190 g kg^{-1}
NaCl	5.4%
NaAlO_2	5.4%
Dissolved Al	1.8%
NaOH	7.4%
K, Ca	ca. $150 \text{ mg litre}^{-1}$
Cr	$0.25 \text{ mg litre}^{-1}$
Cu	$1.05 \text{ mg litre}^{-1}$
Zn	$1.5 \text{ mg litre}^{-1}$
Cd	$0.03 \text{ mg litre}^{-1}$
Pb	$0.4 \text{ mg litre}^{-1}$
Mg, Si, P, Sc, Ti, V, Fe, Ga	$< 4 \text{ mg litre}^{-1}$
Phenol	6 mg litre^{-1}
Cresol	$120 \text{ mg litre}^{-1}$
Xylenol	80 mg litre^{-1}
Cl- and Br-substituted cresol and xyleneol	$< 1 \text{ mg litre}^{-1}$
Aniline	14 mg litre^{-1}
<i>o</i> -toluidine	25 mg litre^{-1}
Substituted anilines	$1\text{--}10 \text{ mg litre}^{-1}$

The Al values are somewhat higher than those reported for the North Sea (between 0.5 and $5.5 \mu\text{g litre}^{-1}$ Al) by Hydes & Liss (1977), and significantly above those for unpolluted Atlantic and Pacific Ocean water (0.5 – $1 \mu\text{g litre}^{-1}$) as reported by Hydes (1979) and the Mediterranean Sea data (0.5 – $4 \mu\text{g litre}^{-1}$) given by Caschetto & Wollast (1979). The dissolved Al content of coastal seawater (at Blankenberge) appeared to vary from 4 to $7 \mu\text{g litre}^{-1}$.

Distribution of pollutants after alkaline aluminate dumping

During the first survey where the research vessel followed the dumping barge at 250 m, the highest pH value, measured 3 m below the sea surface, was 8.42 . The pH of the seawater increased gradually up to about 8.3 during the dumping operation in the whole area affected. The results for the 'dissolved' Al content indicated a maximum value of $465 \mu\text{g litre}^{-1}$; the local concentration at 60 min after the dumping was in the order of 100 – $160 \mu\text{g litre}^{-1}$. A more detailed view as to the variation of 'dissolved' Al as a function of time and depth is shown in Fig. 2. No clear variation of Zn, Ca and Mg could be detected.

The samples taken during the second survey gave a much clearer view on the dilution of the waste cloud immediately after the dumping. The maximum pH encountered was 8.9 (30 m behind the dumping barge); the pH decays continuously down to 8.1 at a distance of 500 m. The maximum local total Al content was $117 \text{ mg litre}^{-1}$ and the Al levels in the wake of the barge dropped steadily to 1 mg litre^{-1} after 500 m. These results for the pH and the Al content in the near surface water as a function of distance from the dumping ship are shown in Fig. 3. A cross section through the waste cloud, taken about 200 m behind the dumping barge, is represented in Fig. 4. It appears that the waste track has a detectable width of about 10 m at 200 m behind the barge; at 500 m it has spread to approximately 30 m diameter.

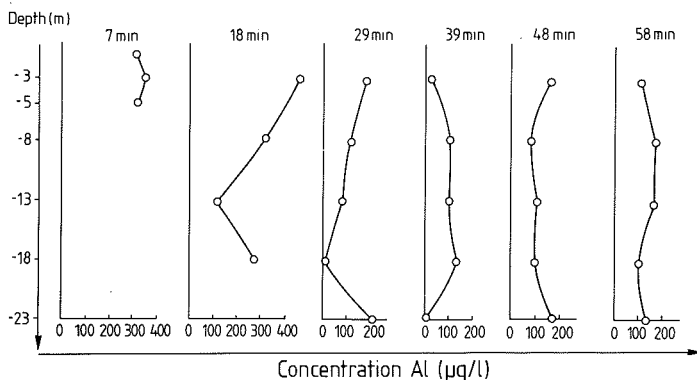
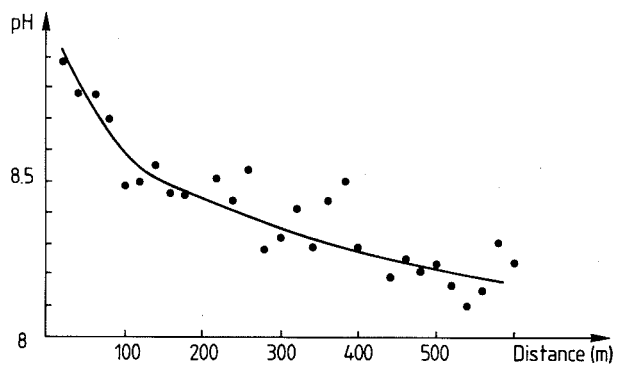
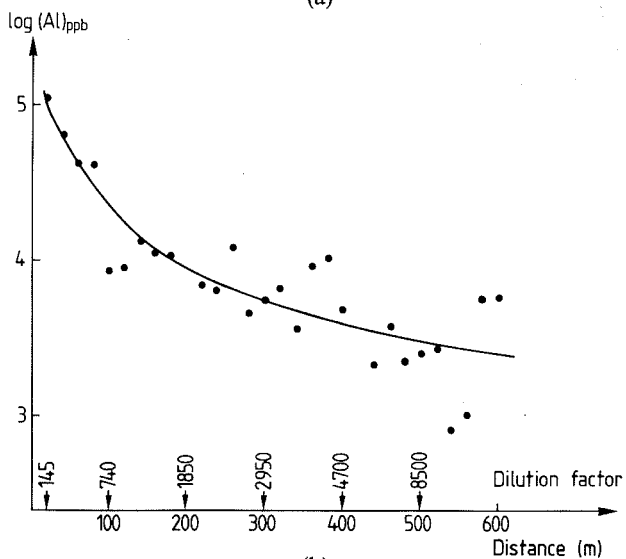


Fig. 2. 'Dissolved' Al concentration as a function of depth and time after the dumping.

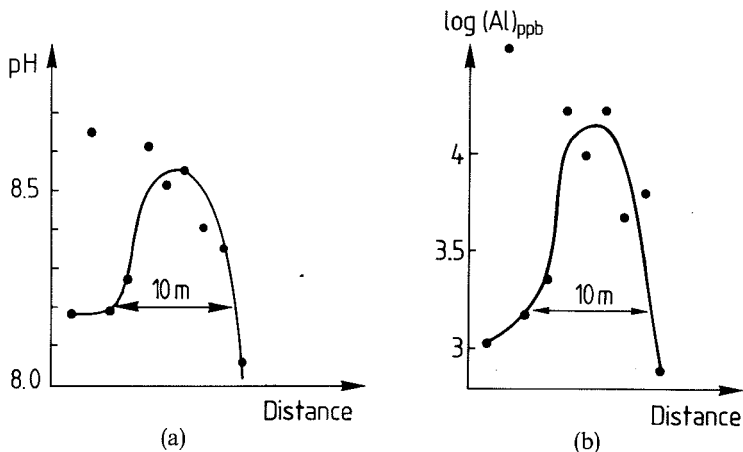


(a)

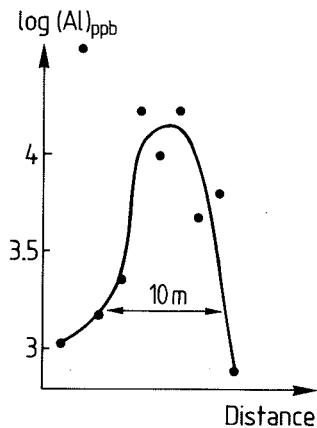


(b)

Fig. 3. Values of (a) pH and (b) total Al content, measured at various distances from the dumping barge in the centre of its wake.



(a)



(b)

Fig. 4. Values of (a) pH and (b) total Al content in a cross section of the waste cloud about 200 m behind the dumping barge.

DISCUSSION

Situation after the dumping

In the wake of the discharging barge, the seawater is visibly disturbed for a relatively long time: a white trace of precipitated matter can be observed several kilometres behind the barge. However, the maximum pH values are below 9, hence clearly below the level where natural life is affected (i.e. pH 10.2 according to Stumm & Morgan, 1970). The highest measured 'dissolved' Al level is only $465 \mu\text{g litre}^{-1}$; the total Al content was locally as high as 117mg litre^{-1} immediately after the dumping but decayed to 1mg litre^{-1} in about 8 min.

From the average Al content of the waste, as given in Table 1, and from the measured total Al concentrations in the wake water, waste dilution factors can be calculated. As indicated in Fig. 3 the dilution factor amounts to about 150 just behind the barge and to approximately 10 000 some 600 m backwards. The initial dilution factor is significantly below that observed for a titanium dioxide waste dumping vessel (Roekens & Van Grieken, 1983) apparently due to a poorer discharge practice.

Relation between waste concentration and seawater pH

The effect of the alkaline aluminate waste on the pH of the seawater was verified in the laboratory by careful titration of natural seawater and of simulated seawater with diluted waste solutions in comparison to pure NaOH solutions, without aluminate. For pure NaOH, after a fast pH-increase, a buffered region is reached around pH 10.3 (corresponding to the second dissociation constant of H_2CO_3 in dilute solutions, as in the dilute buffer against which the glass electrode was calibrated); in this region CaCO_3 precipitates as a white substance. In the presence of aluminate, the situation is drastically different, as shown in Fig. 5. After a sharp initial increase in pH, for both natural and synthetic seawater, one enters a region where there is some buffering (pH 8.5–9) and a white precipitate forms. At a dilution factor (water/waste ratio) around 50, the pH increases sharply again and absolutely no buffering around pH 10.3 or around pH 9.5 (due to precipitation of $\text{Mg}(\text{OH})_2$) is observed. For natural and synthetic seawater very similar results are obtained. It is clear that only at very low dilution levels (below 50) is the resulting pH of seawater above the biological acceptance level. This variation of pH with dilution is quite similar to that reported by Ross & Kodama (1967), who studied the pH change of a 0.1M solution of $\text{AlCl}_3\text{--MgCl}_2$ when titrated with NaOH.

When one uses the relation between dilution and resulting pH and the

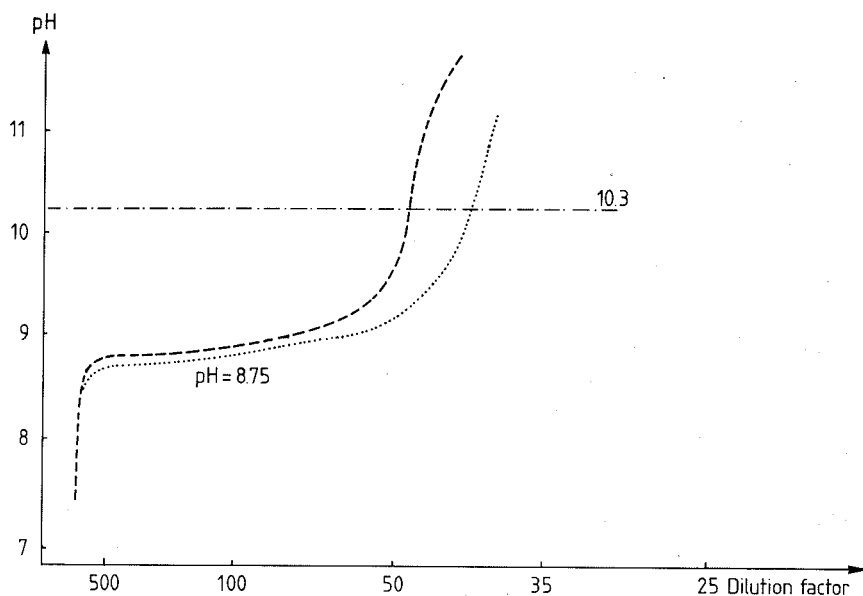


Fig. 5. Variation of pH at titration of natural seawater (-----) and artificial seawater (.....) with alkaline Al waste as a function of the dilution.

data in Fig. 5 to extract waste dilution factors from Fig. 3a, similar results are found as those indicated in the abscissa of Fig. 3b, which were based on total Al levels.

The white precipitate, which was observed at sea and obtained in the laboratory experiments, begins to form at a total Al level of $1.5\text{--}2\text{ mg litre}^{-1}$ in the seawater; or for a waste dilution factor below 10 000.

It was also found in the laboratory experiments that the pH measured for a given seawater/waste ratio, decreases as a function of time. This was also mentioned by Hem & Robertson (1967) who explained it by a further formation of OH-containing precipitate.

Since the data in Fig. 5 were obtained by dropwise addition of the waste to seawater which might not be a representative modelling of massive waste dumping at sea, the influence of the waste addition rate on the pH-change was studied. The measured pH appeared to be higher by 0.3–0.5 pH units for sudden additions. Allowing the waste/seawater mixtures to stand for one day, however, gave roughly the same dilution influence curve as that depicted in Fig. 5. One month later, the pH values had dropped further by about 0.5, showing a buffered region around pH 7.8–8.2, as was found by Ross & Kodama (1967) for titrations of $0.1\text{M AlCl}_3\text{--MgCl}_2$ with 1M NaOH . The gradual pH decrease is indicative of a slow formation of a solid phase rich in OH groups.

Identification of the formed precipitate

The rather high dissolved Al content measured in seawater is not compatible with the very low solubility products mentioned in the literature for pure aluminium hydroxides such as gibbsite; clearly this is not the controlling phase. Less crystalline solid phases such as bayerite are more soluble but still not enough to account for the measured *in-situ* concentration levels of $100\text{--}200\text{ }\mu\text{g litre}^{-1}$ (Smith & Hem, 1972; May *et al.*, 1979). Laboratory experiments carried out over a 6-month period also revealed similar 'dissolved' Al concentration levels in seawater as those measured during the waste dumping event. Indeed, about $300\text{ }\mu\text{g litre}^{-1}$ Al was found in 'solution' at a pH value of 8.4 while a white solid phase was clearly present in the reaction vessel.

The chemical composition of the white solid phase was first investigated by electron probe X-ray microanalysis. Results were obtained for different spots of the precipitate collected on a filter, and for different dilutions; it appeared that the solid phase consists mainly of Mg and Al, with a fairly constant ratio of 2.85–2.20. At elevated pH level, thus at low dilution factors, the relative amount of Mg decreases (magnesium hydroxides are more soluble than aluminium homologues). The solid phase appears as thin flat layers, as seen in Fig. 6. (The precipitate formed by mixing seawater with NaOH exhibits a very different morphology, and it consists of CaCO_3 with H_2O and OH-groups and contains some Mg.) Infra-red analysis then indicated, on the other hand, the presence of OH^- , H_2O and CO_3^{2-} groups in

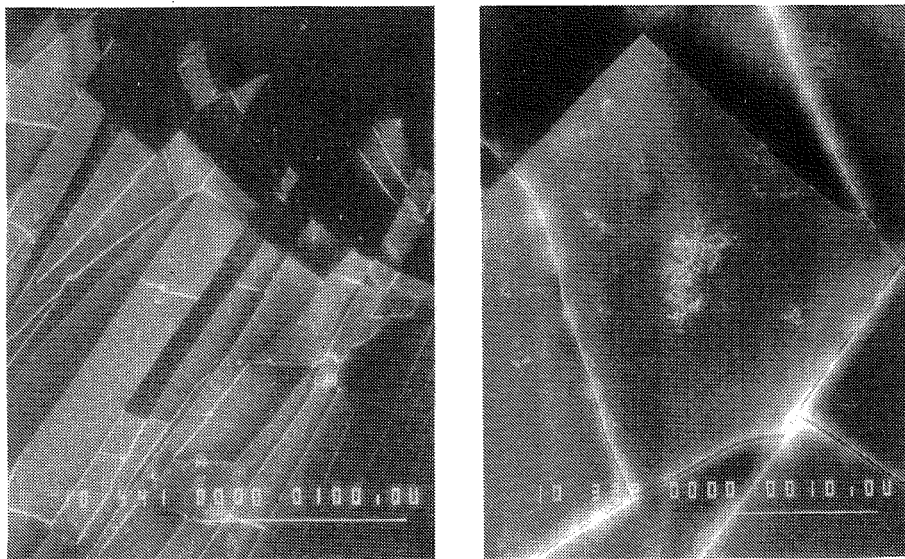


Fig. 6. Electron micrographs of the precipitate formed by the alkaline Al waste in seawater.

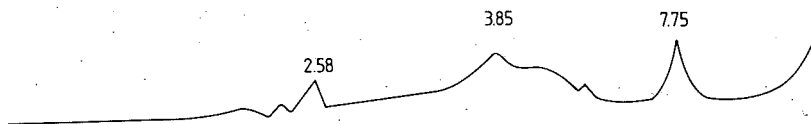


Fig. 7. Diffractogram of the white precipitate after 6 months of aging.

the alkaline aluminate waste precipitate. X-ray diffraction analysis of the dried Mg-Al-rich solid, aged for 6 months, showed a very clear diffraction pattern (Fig. 7); the structure loses its order above 550°C, and no diffraction pattern is found anymore. All these results indicated that the theoretical formula should be $\text{Mg}_6\text{Al}_2\text{CO}_3(\text{OH})_{16} \cdot 4\text{H}_2\text{O}$ with a structure similar to that of the naturally found minerals hydrotalcite and/or mannaseite (ASTM cards 22-700, 14-191 and 14-525). This compound was also synthesized by Ross & Kodama (1967). It consists of two brucite layers, sandwiched by hydrated Al layers with CO_3^{2-} statistically spread over the latter (Fig. 8). The structure was also confirmed by laser microprobe mass analysis; when irradiated by the laser beam the precipitate clearly emits the ions $\text{Al}_x\text{O}_y\text{H}_z^-$ as well as mixed $\text{Mg}_b\text{Al}_x\text{O}_y\text{H}_z^-$ molecular ions. Detailed results of all the measurements of the precipitate are available (Van Grieken & Vandelandnoote, 1985). Since the postulated structure is quite similar to other naturally found claylike minerals, which were reported to be formed in natural seawater systems (Mackin & Aller, 1984) and are invoked to explain the very low amounts of dissolved Al in seawater, we tried to investigate further the

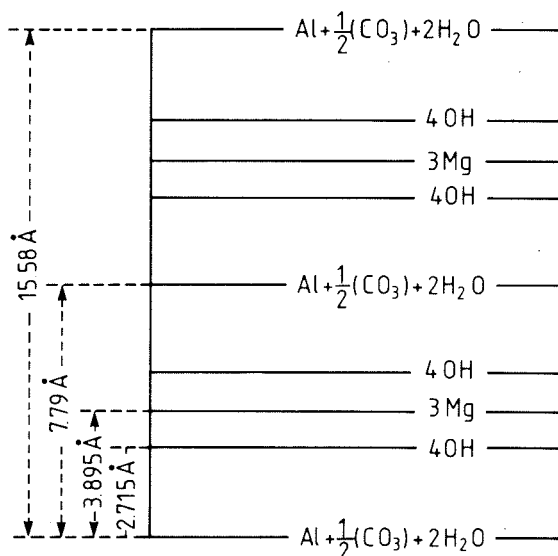


Fig. 8. Possible structure of the $\text{Mg}_6\text{Al}_2\text{CO}_3(\text{OH})_{16} \cdot 4\text{H}_2\text{O}$ precipitate (after Ross & Kodama, 1967).

reactions that these hydrotalcite-like mineral phases may undergo under natural conditions. Suspension of minor amounts of the formed solid phase in seawater revealed that after a 4-day period, the ratio between Mg and Al is lowered (down to 1 approximately) while important amounts of Cl and S (probably SO_4^{2-}) are absorbed. The precipitate can also react with silicate-containing solutions and a solid phase is formed with nearly equal amounts of Mg, Al and Si. From X-ray diffraction experiments, one can see that the original structure is then still present.

Kinetics of the precipitate formation

Laboratory experiments were also carried out to study the kinetics of the precipitate formation. Waste liquid was mixed with unfiltered seawater. For high waste/seawater dilution factors (above 50 000) the dissolved Al concentration remained constant ($220\text{--}350\text{ }\mu\text{g litre}^{-1}$ Al and pH 7.5–8) for a long time; no precipitation was observed. At intermediate dilution (10 000–50 000), the initial 'dissolved' Al concentration of $1400\text{--}2600\text{ }\mu\text{g litre}^{-1}$ decreased to $200\text{--}400\text{ }\mu\text{g litre}^{-1}$ after an induction period of 30–200 min. At low dilution (below 10 000), the precipitate is formed immediately and results again in eventual 'dissolved' Al levels of $200\text{--}400\text{ }\mu\text{g litre}^{-1}$. For dilutions between 50 and 500, similar 'dissolved' Al concentrations were measured even after a 6-month delay. Clearly reduction of the Al concentration to background levels requires transformation of the $\text{Mg}_6\text{Al}_2\text{CO}_3(\text{OH})_{16} \cdot 4\text{H}_2\text{O}$ to more crystalline $\text{Al}(\text{OH})_3$ or to clay-minerals. It was noted, in experiments with filtered seawater, that the presence of condensation nuclei is a very important factor in this context.

Composition of the sediments in the dumping area

The particle-size distribution in a transect from the centre of the dumping area downstream was similar to that in the reference samples (approximately 56% of the particles above 0.4 mm diameter, 43% in the 0.2–0.4 mm range, and approximately 1% below 0.2 mm). The chemical composition of individual particles smaller than $100\text{ }\mu\text{m}$, as investigated with automated electron microprobe analysis in combination with multivariate numerical analysis (Bernard *et al.*, 1986), indicated a clay-like composition for most particles, and approximately 15% quartz particles in all samples; the only difference relative to the reference sample was the higher abundance of CaCO_3 particles, which decreased steadily from 37% in the dumping area to approximately 10% further away. Electron micrographs of these CaCO_3 particles indicated conglomerates of $1\text{ }\mu\text{m}$ subparticles. X-ray diffraction analysis showed quartz, calcite, illite and traces of chlorite in all samples

and in the reference sediment. This is in agreement with earlier results of Van Nieuwenborgh (1982) for the same area. Newly formed $\text{Mg}_6\text{Al}_2\text{CO}_3(\text{OH})_{16} \cdot 4\text{H}_2\text{O}$ precipitate could thus not be detected with certainty, either because it is weakly structured or it is efficiently carried away from the dumping area or it reacts with or attaches to clayey material which is abundant in the area.

CONCLUSION

The dumping of 1000–2000 tonnes alkaline Al waste, containing about 7% NaOH and 2% dissolved Al, leads to a maximum local pH of 8.9 and total Al concentration up to $120 \text{ mg litre}^{-1}$ in the 10-m wide track just behind the discharging barge corresponding to a waste dilution factor of 150. This decays to pH 8.1 and 1 mg litre^{-1} Al in the 30-m wide track at 500 m behind the ship. A white precipitate is formed immediately; its composition is probably $\text{Mg}_6\text{Al}_2\text{CO}_3(\text{OH})_{16} \cdot 4\text{H}_2\text{O}$. No clear trace of this compound is found in the sediments of the dumping area.

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