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Effects of acid-iron waste disposal in the marine environment

by

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SUMMARY: The effects of acid-iron wastes left in the production of titanium dioxide in the marine environment are reviewed. Results of the investigations in the New York and German Bights and at the Norwegian coast reveal that these wastes can be discharged without producing major harmful effects (1) if dilution after discharge is high (2) if no accumulation of wastes in the discharge area takes place and (3) if other ecological factors are favourable.

A. INTRODUCTION

Acid-iron wastes are by-products in the manufacturing of titanium dioxide, which is the most commonly used white pigment. The total TiO_2-production of the world was about 2.5 million tons in 1972. It can be assumed that more than 50 % of the residues from the fabrication of TiO_2 are discharged into the sea or near-shore waters. Usually TiO_2 is produced from titanium iron ore (ilmenite) by dissolving the ore using sulfuric acid. By this process acid-iron wastes of different concentrations are left; they contain about 6-19 % H_2SO_4, 5-15 % $FeSO_4$ and low quantities of mineral pollutants. As an example, the composition of the wastes discharged into the German Bight near Helgoland is given in table I.

These wastes are produced by a factory located near Bremerhaven, the annual production of which is about 36,000 tons TiO_2 leaving then 650,000 tons of the wastes.

Dumping sites in the North Sea and the known quantities of wastes discharged are shown in figure I. Quantities dumped into the New York Bight (more than 2.5 million tons per year, VACCARO et al., 1972) are similar to those dumped into the North Sea; more than a million tons per year are discharged by a factory in Italy into the Tyrrhenian Sea (RENZONI, 1973), and 20,000 to 40,000 tons of iron are discharged together with acid at Cyprus (GFCM, 1972).

Research on fate and effects of these wastes has been carried out by several institutes, especially on wastes dumped into the New York Bight, the German Bight and at the Norwegian coast. This paper reviews the results of these research activities.

B. CHEMICAL AND PHYSICAL FATE OF THE WASTES IN THE SEA AFTER DISCHARGE

Sulfuric acid, when mixed with sea water, will reduce its pH, which is 8.1 to 8.2 normally. If dilution is rapid, the buffering capacity of the sea water will be sufficient to neutralize the acid, by which the CO_2 partial pressure will increase for some time. Ferrous sulfate will increase the iron concentration in the sea water; Fe^{2+} will be oxidized to Fe^{3+} as soon as the pH rises again, and the iron will precipitate as hydroxide. By the oxidation of the Fe^{2+} an O_2 deficit will be caused in the sea water. The ferric hydroxides (or ferric oxide-hydrates) remain in suspension making the water turbid; because of its density the ferric hydrocide will sink downwards in the water column.

Provisions for quick dilution after discharge have been made to restrict harmful effects of the concentrated wastes in the New York Bight as well as in the German Bight and off the Dutch coast, where the wastes are discharged from moving tankers into the wakes at water depths of more than 20 m. These waters are influenced by turbulence and currents, so that the wastes can be diluted in large volumes. Initial dilution was found to be 1 : 250 (ca. 150 mg Fe/l) and higher in the New York Bight (REDFIELD & WALFORD, 1951) and about 1 : 1000 (ca. 50 mg Fe/l) off the Dutch and German coasts (Waterloopkundig Laboratorium et al., 1970; WEICHART, 1972a). A secondary dilution factor of about 10 was calculated from the iron concentrations for the first hour after discharge by WEICHART (1972a), and it was about 2 in the second hour at medium turbulence conditions and medium current velocity in the German Bight. Minimum dilution for the wastes reaching the sea bed at 20 m depth was calculated to be more than 1 : 5000 by the Dutch investigators.
The dilution of teh less concentrated wastes from the titanium dioxide factory at the Glåma estuary in Norway is at least 1 : 1000 (1.4 mg Fe/l) and possibly 1 : 7000 a few km from the point of discharge due to high water transport in this estuary (Bokn et al., 1974).

A decrease in pH was found to be restricted to the wake waters within the first four minutes only after the release (REDFIELD & WALFORD, 1951: New York Bight; WEICHART, 1972a: German Bight). WEICHART recorded the pH of the water 20 cm above the sea bed at the discharge site in about 28 m depth continuously for four weeks. He did not find any change of the pH near the sea bed, although the tanker passed over the instrument during discharge.

Only 3-4 % of the oxygen content of the waters in the New York Bight, into which the wastes were introduced, were consumed by the oxidation of the ferrous ions (REDFIELD & WALFORD, 1951). In the German Bight the oxygen content of the polluted water returned to normal during the first hours after release (WEICHART, 1972a).

The iron concentrations resulting from permanent discharge are constantly higher in the waters within and around the disposal areas than in neighbouring areas of the New York Bight as well as the German Bight (REDFIELD & WALFORD, 1951; National Marine Fisheries Service Report, 1972; WEICHART 1972 a, b). Iron content of the Norwegian Hvaler Archipelago surface waters is also increased due to the pollution from the Glåma estuary (ARNESEN, 1969). In the German Bight the concentrations measured 5 m below the surface (0.5 mg/l at the highest) are similar to those measured in the near-shore areas polluted by the rivers Elbe and Weser.

The iron concentration in the near-bottom waters was shown to increase only several hours after discharge (WEICHART, 1972 a). But, as all these areas inspected are influenced by currents, there is little or practically no further accumulation of iron at the places of discharge. Loose masses of ferric oxide-hydrate flakes can be seen floating above the sediment when taking bottom samples during calm days in the German Bight discharge area; such iron particles were also found fixed to the mucus of polychaete tubes (RACHOR, 1972). No considerable incorporation of the iron, however, could be detected in the sediments in and around the discharge area (WEICHART, 1972a; NAUKE, 1971 - personal communication; RACHOR, 1972 and new,

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unpublished results). In comparison to other places in the German Bight, concentrations of near-bottom seston including iron were high at stations north-east and in the centre of the discharge area (WELLERSHAUS & RACHOR, unpublished preliminary data from 1971). Similar to the situation in the New York Bight (VACCARO et al., 1972), most of the iron masses must be transported out of the area by bottom currents. Whilst no significant accumulation of iron within the sediments of the New York and German Bights was proven, a moderate increase in iron content in the uppermost sediment layers was detected in the Norwegian Hvaler area (BOKN et al., 1974).

In all these cases, dilution of the acid-iron wastes was found to be relatively high - minimum persistent dilution in the New York Bight area being about 1 : 39,000 with 0,8 mg Fe/l (VACCARO et al.) and in the German Bight about 1 : 100,000 (calculated from 0,5 mg Fe/l found be WEICHART, 1972a) - and there is little or no further accumulation of iron in the respective areas. Acidification of the water and oxygen consumption are of limited ecological significance. It is clear that comparable results can only be expected, if dumping or release of acid-iron wastes is carried out in areas influenced by turbulence, currents and of adequate depth.

It is likely, however, from the investigations in the New York Bight (VACCARO et al., 1972) that the large quantities of iron discharged will accumulate in other areas, where fine sediments will be accumulated by natural phenomena. Furthermore, it must be kept in mind, that other heavy metals have been found to accumulate in these areas, too, and that even the sediments in the discharge area as well as plankton and benthos were found to have slightly raised heavy metal contents.

C. BIOLOGICAL EFFECTS OF THE ACID-IRON WASTES ON MARINE ORGANISMS

I. P l a n k t o n :

Laboratory studies: Results of the studies on the effects and toxicity of acid-iron wastes are somewhat difficult to compare, since different waste compositions were used. To facilitate comparison,

the Fe-concentrations of the dilutions used are indicated.
Growth of marine phytoplankton algae was found to be reduced in dilutions of the wastes with ca. 15 mg Fe/l (KAYSER, 1970), ca. 8 mg Fe/l (ARNESEN et al., 1973) and even ca. 1.2 mg Fe/l only (KAYSER, 1969). But, no adverse effects on growth and species diversity were detected in mixed cultures of 4 diatom species in a 1 : 10,000 diluted acid-iron waste medium with ca. 3.0 mg Fe/l (VACCARO et al., 1972). This concentration is four times greater than the maximum observed to be persistent in the New York Bight discharge area.
Cladoceran crustacea, which were kept in suspensions of ferric hydroxide for five days (KETCHUM et al., 1958), were not affected, although their guts were crammed with the hydroxide. Copepods, however, failed to reproduce or showed delayed development at a concentration of 1 : 10,000 (ca. 3.0 mg Fe/l) of the wastes, but were not affected at concentrations of 1 : 100,000 (VACCARO et al., 1972). GRICE et al. (1973) found adverse effects on copepods, too, but in higher concentrations (1 : 5000, ca. 6 mg Fe/l). Their results indicated that the acidity of the test solutions may be the principal cause of the adverse effects shown.
ARNESEN et al. (1973) discuss the effects of acidification and point aut that heavy metals can be more harmful at low pH. Thus, it seems possible that acidity is not the only cause of adverse effects. Moreover, KINNE & SCHUMANN (1968) found larvae of molluscs and crustacea to be hindered in their movements by ferric hydroxides.

In situ studies: REDFIELD & WALFORD (1951) and KETCHUM et al. (1958) reported an instantaneous damage of zooplankton directly in the wake of the discharging barge in the New York Bight; but such effects were of very little ecological significance, as they were found to be restricted to relatively small water masses. VACCARO et al. (1972) observed that the standing crop of zooplankton in the discharge area was 30 per cent less than that of a control area; but this finding was attributed to large scale patchiness of zooplankton in the New York Bight and could not be explained by influences of the wastes. A more detailed zooplankton study of WIEBE et al. (1973) supports these conclusions. It is probable that harmful effects as shown in the laboratory studies are confined to the less diluted small water bodies in the wake of the discharging ship. The persistent concentrations of waste in the New York discharge area are not sufficient to bring about distinct large scale negative effects on zooplankton.

II. B e n t h o s

Laboratory studies: Long-term experiments of WINTER (1972) with the mussel, <u>Mytilus edulis</u>, revealed harmful effects of ferric hydroxide suspensions in low concentrations (1.0 mg Fe/l) at food concentrations below optimum (personal comm.), probably due to interference with the feeding processes. ÅKESSON (1970) demonstrated adverse effects of sulfuric acid on growth and mortality rates of the polychaete worm <u>Ophryotrocha labronica</u> at concentrations above 40 ppm. Germlings of the red algae <u>Ceramium strictum</u> were not affected by wastes diluted at 1 : 500 (ca. 8 mg Fe/l) in experiments conducted by ARNESON et al. (1973).

In situ studies: Benthic organisms, which are less motile and thus more exposed to continuous waste disposal than, for example, fishes and plankton, have been studied in several acid-iron waste discharge areas.
Investigations about epibenthic animals as well as infauna in the New York Bight (ARNOLD & ROYCE, 1950) did not show effects attributable to the wastes. In a survey after 22 years of dumping, VACCARO et al. (1972) found the numerical abundance of benthic animals in the discharge area to be lower than in a control area, but there were no significant differences in biomass or species diversity. The effects of the acid-iron wastes were assumed to be none or to be minimal in respect to numerical abundance.

The benthic macrofauna in the discharge area in the German Bight had been assessed before the beginning of discharge by STRIPP & GERLACH (1969). The fauna belonging to the Venus-gallina-community was shown to be of minor productivity. Since the beginning of waste discharge in May 1969, the benthic fauna has been investigated regularly, but harmful effects have not been proven to date (RACHOR, 1972 and unpublished results). The fauna was found to fluctuate very much numerically as well as in terms of

biomass. The low biomass values of STRIPP & GERLACH (1969) do not seem to be representative for longer periods. Species composition, diversity, reproduction and production of the fauna have not shown trends which could be attributed to any impoverishing harmful effect of waste discharge. Even benthic animals with planktic larvae showed normal recruitment. A study on the amphipod, Ampelisca brevicornis, showed that its population was not affected (KLEIN, 1973). But, it seems possible that the fluctuations of other species in the discharge area may be modified by the wastes.
Investigations about the nematode fauna in the discharge area have not indicated any bad effect, too (LORENZEN, 1974).

Residual wastes of low concentrations (up to 38,000 m^3 per day with less than 0.2 $^o/oo$ $FeSO_4$ and 0.7 $^o/oo$ H_2SO_4) from the TiO_2-factory near Bremerhaven are released into the Weser estuary in a region under salinity and other pollution stress. MICHAELIS (1973) found the intertidal brackish water fauna in just this region to be impoverished, possibly due to pollution stress.

The Norwegian Hvaler area as a whole does not seem to be seriously affected by pollution (BOKN et al., 1974), but there are indications of negative effects near the discharge place in the Glåma estuary: Some deposit feeding bottom animals are absent near the river mouth, and the algal flora seems to be reduced, possibly due to deposits rich in iron. BOKN et al., however, argue that the acid-iron waste could be a possible explanation, but that salinity and other pollutants are also important factors.

III. F i s h e s :

Laboratory studies: Embryos and larvae of herring (Clupea harengus) were adversely affected by wastes diluted at 1 : 32,000 (ca. 2 mg Fe/l (KINNE & ROSENTHAL, 1967). Sublethal effects on young Solea solea and Gobius pictus were demonstrated at similar concentrations (KINNE & SCHUMANN, 1968). HALSBAND (1968) found adverse effects of slightly diluted acid-iron wastes (concentrations not published) on fishes of fresh, brackish and sea waters.

In situ studies: Investigations on influences of the acid-iron waste discharge upon species diversity and abundance of fishes in the discharge area near Helgoland and in 4 comparison areas did not prove any change attributable to the wastes (DETHLEFSEN, 1973). These results are in agreement with those obtained in the New York Bight (REDFIELD & WALFORD, 1951; review: see KNUTZEN, 1972). In the report of the ICES working group on pollution of the North Sea (1969) no bad effects of acid-iron waste discharge on fishing interests near the Belgian coast were stated.

D. CONCLUSIONS

From the investigations reviewed it can be concluded that acid-iron wastes from titanium dioxide production have not brought about major negative effects in the marine environments studied. This is in all probability due the effectiveness of dilution in the waters studied, which is mainly achieved by favourable turbulence, currents, depth and other hydrographical factors and supported by releasing the wastes directly into the wakes of the moving dumping vessels. Harmful effects as shown by several experimental studies could not be established in situ. There are, however, hints especially from the Norwegian estuarine discharge area that acid-iron wastes can gradually menace the marine environment. Such an impairment can be caused if hydrographical and other conditions are not optimum, especially if other ecological stress factors are involved (e. g. pollution stress). Thus, it seems possible that acid-iron wastes dumped in such marine areas can affect life considerably, as, for instance, assumed for the Mediterranean by RENZONI (1973).

In the report of the US National Marine Fisheries Service (1972) on the effects of waste disposal in the New York Bight, it is demonstrated that solid waste disposal can bring about quite different effects in marine environments, which differ in respect of their hydrographical conditions. If provisions as described in all the cases of acid-iron waste discharge are not made, it is likely that other near-shore dumping areas could be endangered, especially since the quantities of TiO_2 produced in the world are large and still increasing.

Furthermore, it must be stressed that ferric hydroxide particles can adsorb other substances, by which organic nutrients as well as noxious matter will be enriched: It was shown, for instance, by VACCARO et al. (1972) that heavy metal content of sediments and animals from the New York Bight discharge area was higher than from the control area. The fluctuations of several macrobenthic animal populations in the German Bight discharge area could be influenced by nutrient-enriched near-bottom seston available during calm weather periods.

Discharging of acid-iron waste into the endangered marine environment does not seem to be the best way to get rid of it. The quantities of the wastes can partly be reduced by recycling the sulfuric acid (for dissolving the ilmenite ore), or, by extracting the iron from the ferrous sulfate. Furthermore, the wastes seem to be useful in waste water treatment and fertilizer production. In the future it can be expected that alter-ations in the fabrication procedure of titanium dioxide will reduce the large quantities of wastes produced (s. NESPITAL, 1973).

As long as dumping of acid-iron wastes in the sea is regarded to be necessary, the following precautions are required:

(1) Discharge should be carried out in areas with low importance for fisheries, because negative effects on organisms cannot be excluded as shown by experimental studies.

(2) The toxicity of the concentrated wastes requires rapid and efficient dilution (about 1 : 10,000 one hour after discharge).

(3) If disposal of the wastes cannot be achieved in a very restricted area (as, for instance, in the case of red mud disposal near Marseille, BOURCIER & ZIBROWIUS, 1973), appreciable accumulation of ferric hydroxides and of sulfates in the water and in the sediments of larger areas should be avoided.

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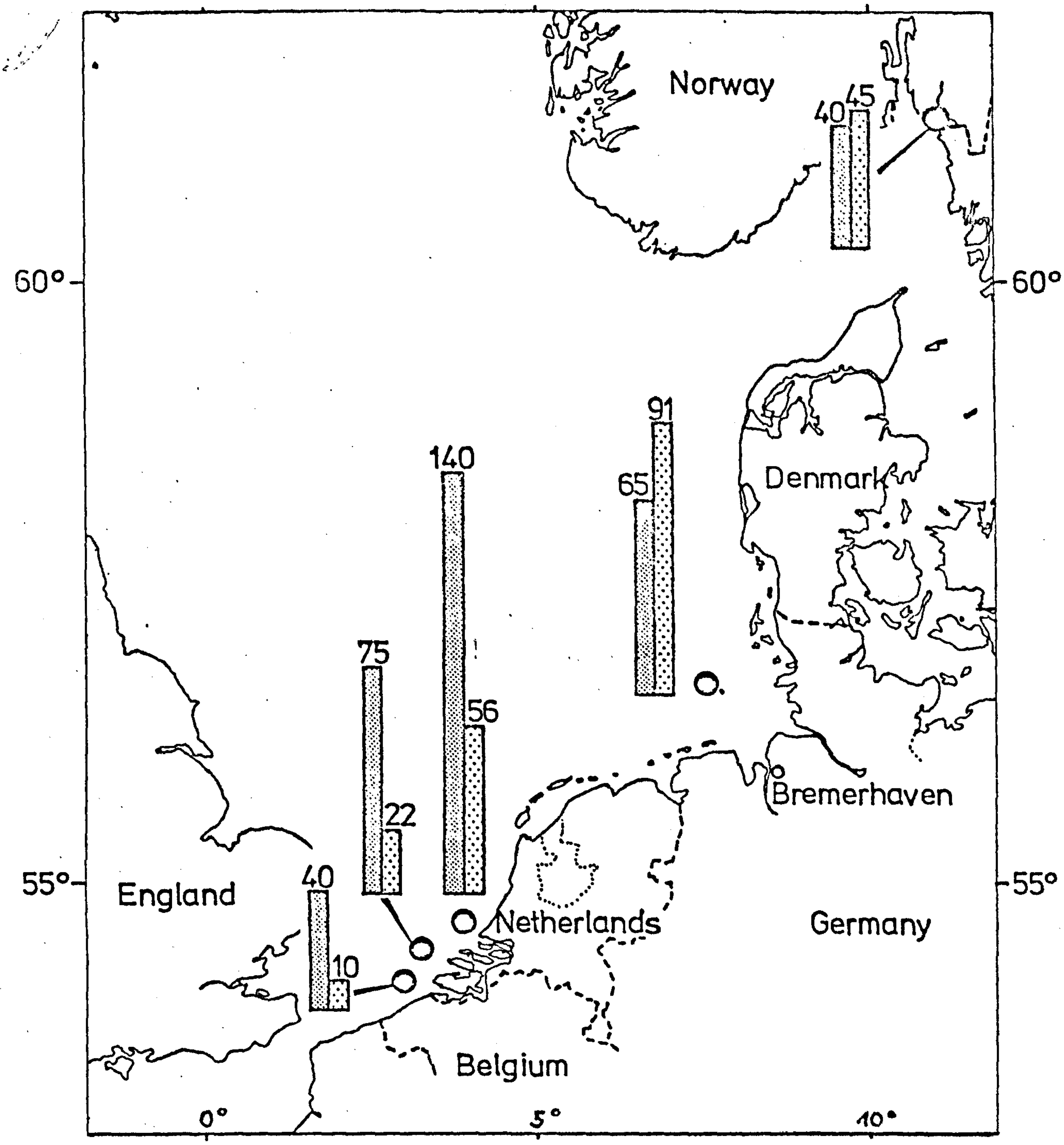

Fig.: Sites of acid-iron waste discharge in the North Sea. Heavily dotted bars: 1000 tons of sulfuric acid per year, light dotted bars: 1000 tons of ~~iron~~ ferrous sulfate per year.

Table I.

Concentrations of main components of the acid-iron wastes discharged into the German Bight (1969-1973), according to figures compiled by the Titangesellschaft mbH, Nordenham:

Component	Concentration (per cent)
H_2SO_4	ca. 9 - 10
$FeSO_4$	ca. 13 - 14
TiO_2SO_4	ca. 1.4
$MgSO_4$	ca. 1.0
$Al_2(SO_4)_3$	$<$ 0.2
$MnSO_4$	ca. 0.07
$CaSO_4$	$<$ 0.07
$VOSO_4$	ca. 0.05
$NaSO_4$	$<$ 0.03
$Cr_2(SO_4)_3$	ca. 0.01
H_2O and traces of other elements[+]	remainder

[+]other components can be Zn, Pb, Co, Ni, Cu, Cd, as found by VACCARO et al. (1972) in the wastes discharged into the New York Bight and KNUTZEN et al. (1974) in the wastes from Norway.