

SULPHATE MINERALISATIONS FROM THE DUMPS OF THE FORMER EMMA AND HENDRIK COLLIERIES (SOUTHERN LIMBURG, THE NETHERLANDS)

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Bongaerts, Hans L. Sulphate mineralisations from the dumps of the former Emma and Hendrik collieries (southern Limburg, The Netherlands). — *Contr. Tert. Quatern. Geol.*, 30(1-2): 3-17, 5 figs, 4 tabs, 3 pls. Leiden, June 1993.

During excavation of the dumps of the former Emma (Treebeek) and Hendrik (Brunssum) collieries, sulphates have been found to occur commonly and comprise thenardite, gypsum and a jarosite-type of mineral. During dry periods, thenardite occurs locally as crusts and overgrowths; it originates from the continual removal of Na ions. In order to define jarosite, chemical as well as X-ray diffraction (XRD) analyses were made, which showed this to be a mixed Na, K, H₂O jarosite, its crystal habit being comparable with K jarosite (Joint Committee of Powder Diffraction [JCPD] map 36-427). Amongst the waste products at the dumps, jarosite is found as crusts with spherical extensions, bright yellow to light brown in colour. Gypsum (occasionally associated with jarosite) occurs especially in well-developed euhedral crystals in the Carboniferous shales and on concretionary siderite nodules; its crystal morphology is described. Jarosite and gypsum are typical products of pyrite oxidation, which mineral is either finely distributed or occurs as larger-sized concretions in the rock. In addition to mineralogical data, the results of pH measurements are presented. Following a brief account of the structure of the waste dumps is a tabulation of all secondary minerals of the Dutch collieries known to date.

Key words — Sulphate mineralisations, thenardite, jarosite, gypsum, waste dumps, collieries, southern Limburg, The Netherlands.

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INTRODUCTION

In view of the fact that large-scale excavations are currently being carried out at the Brunssum dump (Fig. 1), it was decided to look more closely into the occurrence of oxidation products of iron sulfides and carbonates which are found in large numbers in the Carboniferous shales dumped there. Collected also were primary Zn-Pb-Ni minerals, which qualitatively match the specimens previously described from *in situ* occurrences in the collieries concerned (Bongaerts, 1992). On these sulfides, no secondary minerals could be determined. The sulfides are part of an extensive mineral range, the most important

constituents being galena (PbS, cubic) and sphalerite (ZnS, cubic).

On German territory, extensive amounts of ore minerals occur close to the surface, which has resulted in long periods of active mining. This is one of the reasons why this area has been the subject of mineralogical studies (*e.g.* Klockmann, 1910; Gussone, 1964) for some time. On Dutch territory, such lead-zinc mineralisations were exposed in the former collieries (*see e.g.* Kimpe, 1948), but have also been recorded from several boreholes (Friedrich *et al.*, 1987) and been demonstrated in geochemical studies near Epen (Dijkstra & Bot, 1968). Iron sulfide and carbonate minerals occurring in these Late Carboniferous rocks are primarily of syngenetic origin, being unrelated to tectonic faulting (Kimpe, 1980). The occurrence of secondary minerals, originating from hydrothermal ores or syngenetic minerals, has but rarely been recorded in the literature (Driessen, 1962).

Sulfides from Carboniferous pyrite-bearing rocks in Belgium were studied by van Tassel (1973), who provided XRD data for all mineral species described. In Germany, research into secondary minerals was conducted by Seeliger (1950), who

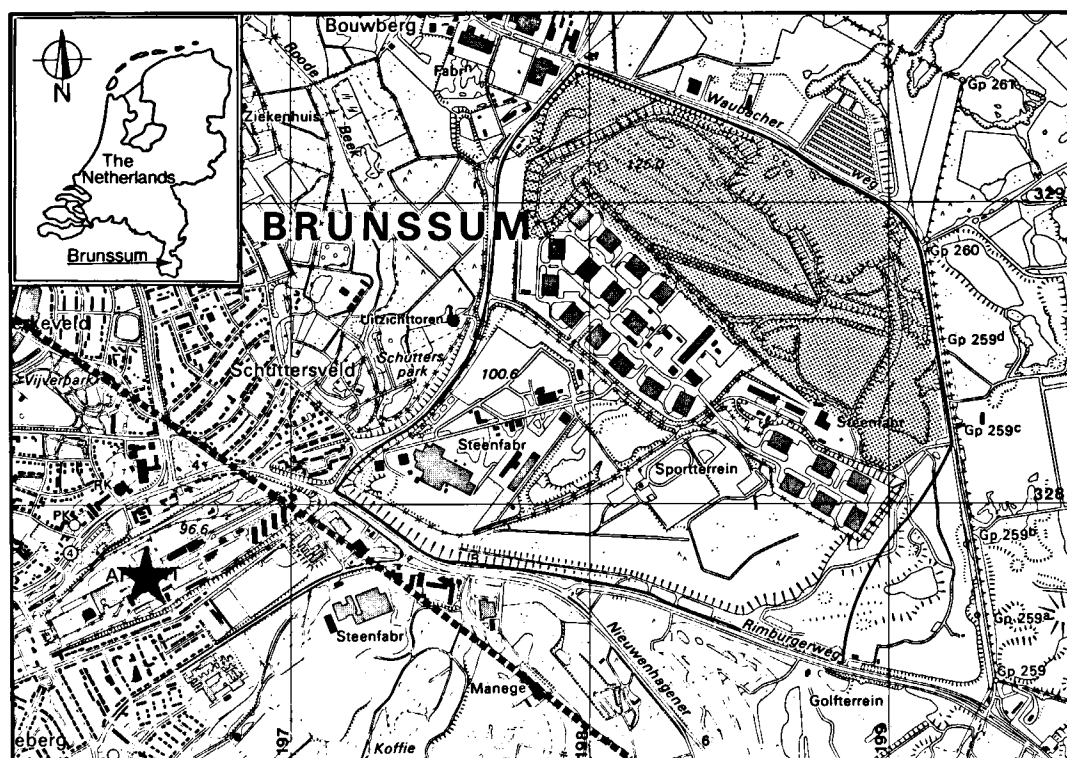


Fig. 1. Map showing location of Emma/Hendrik waste dump; the line indicates the maximum extent of the dump, now partially excavated. The shaded area is the part investigated, and currently excavated. A star indicates the former above-ground buildings of Staatsmijn Hendrik, the stippled line denoting the course of the most important Dutch fault, the Feldbiss. Copyright: Topografische Dienst, Emmen.

described many species from the Ruhr mining district; in a number of cases, however, I doubt if these in fact represent secondary mineralisations. A more recent study of minerals occurring on waste dumps of German collieries is by Grünhagen (1982).

Zodrow (1980, 1989), Zodrow & McCandlish (1978) and Zodrow *et al.* (1979) described products of pyrite oxidation from the extensive Late Carboniferous Sydney Coalfield of Nova Scotia (Canada). Thirty-six sulfide types were identified by means of XRD, chemical analyses, Differential Thermal Gravimetry [DTG] and Scanning Electron Microscopy [SEM] (Zodrow, 1989).

Below, data on the mineralogical characteristics of all sulfides recognised, and the pH course of part of the Brunssum dump are presented. In the north-eastern corner, exposures are most easily accessible (Fig. 2), which explains why all data presented below are based on that part of the dump. All illustrated minerals are in the author's private collection, while a number of thenardite, jarosite and gypsum samples have been donated to the mineralogical collections of the Natuurhistorisch Museum

at Maastricht (The Netherlands), registration numbers NHMM 1993051-052 (jarosite), 1993053-054 (thenardite) and 1993055 (gypsum).

HISTORY OF THE DUMPS

Sulphate genesis is closely related to the amount of rock debris dumped, which has an influence on the pressure and density of the basal part of the dump in particular, and to dumping methods. Interim activities, amongst which are excavations, may change the course of the oxidation process. For the picture to be as complete as possible some remarks on the structure and excavation of the dump are necessary:

The dump is situated east of Brunssum (Fig. 1) where Miocene fluvial sediments assigned to the Kiezeloöliet Formation are exposed. The dump consists of rock debris of the former Emma and Hendrik collieries (Pl. 1), where coal was quarried from rocks of Westphalian age between 1917 and 1964 (Hendrik, subsequently merged with Emma) and 1919 and 1973 (Emma). The term 'Terreinen steenstort' as used by the Dutch State Mines (DSM)

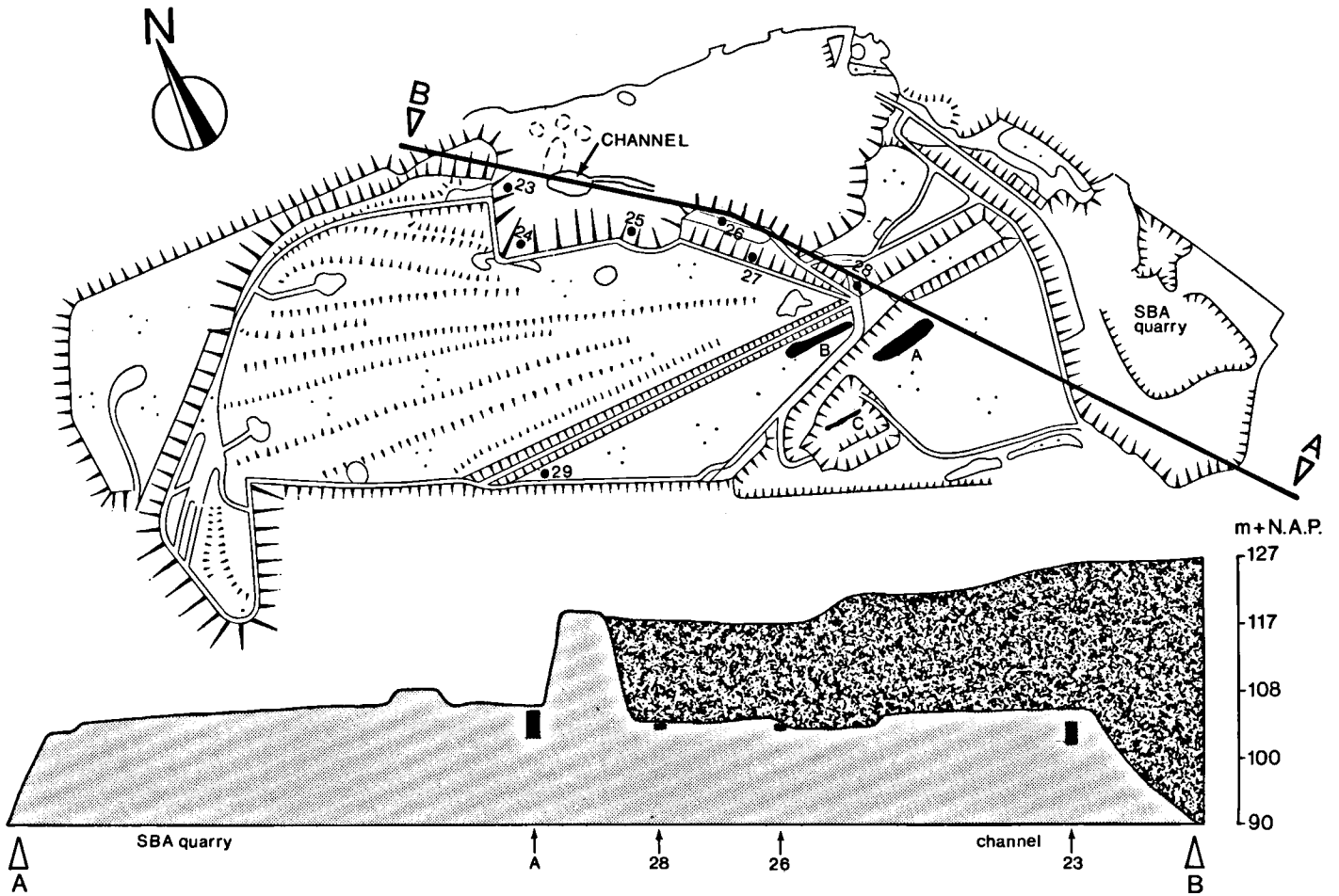


Fig. 2. Upper figure: topographical situation of the studied part of the dump, scale 1:10,000, 1990. Copyright: Topografische Dienst, Emmen. Lower figure: section, horizontal scale 1:8,000, vertical scale 1:1,000, 1974 (with maximum height reached). The measure points indicated correspond to those in Fig. 3.

comprises amongst others settling basins, rails and timber yards. The areal extension of the dump itself initially comprised 180 hectares (Hoefnagels, 1974), the maximum height 37 metres. It started at the extreme western end of the site. The extension of rails in a northeasterly direction in 1922 saw an important expansion of the dump. Post-war dumping concentrated on the northern part. From c 1965 onwards it reached its final shape and size, a typical plateau-like dump.

Extensive fires, such as the one that destroyed part of the Maurits dump, have not occurred at this site, but smaller fires have been recorded. Exothermal energy originating from pyrite oxidation may lead to a temperature rise, which results in spontaneous combustion in the dump interior (Kuyt, 1960). Various temperature measurements have been performed at the Brunssum dump: a series of

measurements in 1973 at 2 metre depth revealed a minimum temperature of 95°C and a maximum of 140°C. However, these temperatures are quite low, when compared with other dumps in southern Limburg for which temperatures of 500°C are recorded in the literature. The sulphates described below have been collected from unburnt rocks.

NEWLY FORMED SUBSTANCES OF THE DUTCH LATE CARBONIFEROUS

Pyrite (FeS_2 , cubic) and marcasite (FeS_2 , orthorhombic) are both minerals occurring in a very delimited stability field. Both species are thus on dumps a potential source for sulphate genesis. A limited amount of industrial waste in the form of ferrometals has been noted during field work. These products may also lead to the genesis of newly for-

med substances. Most of the sulphate minerals, however, originated from chemical reactions of iron sulfides (which generally are finely distributed in the rock) and, to a lesser degree, of iron carbonates.

The genetic relationships amongst these newly formed substances of former Limburg collieries is summarised in Table 1.

PRIMARY FE MINERALS

To account for the elements necessary for jarosite and gypsum genesis, the following process may be considered (compare Wiggering, 1986): Fe ions come into contact with S (pyrite) and the complex anion CO₃⁻² (siderite, FeCO₃). The anion SO₄⁻⁴ resulted from the oxidised S cations of pyrite. Thus, this mineral species is here of prime importance in sulphate genesis. Dissolved Ca⁻² ions stem from the neighbouring shales. Gypsum is primarily concentrated on the splitting planes of these shales. The

iron carbonate siderite (see e.g. Teodorovich, 1961) occurs commonly in Carboniferous rocks. The crumbly concretions collected from the dump exhibit a spherical erosion form, the splitting planes of which are often filled with gypsum. Siderite is a syngenetic mineral in these shales and coal seams, which generally occurs in clayey siderites, of irregular shape (Kimpe, 1980; see Pl. 2, Fig. 1).

Pyrite is also a common constituent of Carboniferous rocks (Berner *et al.*, 1979; Curtis, 1967). The mechanism behind pyrite genesis was described in detail by Berner (1969), to which paper the reader is referred. Pyrite occurring in rocks in Limburg is syngenetic in nature but is found also, but less often, to form part of lead-zinc mineralisations (Kimpe, 1980).

Syngenetically formed crumbly crystal aggregates and concretions of pyrite have been described (Kimpe, 1948, 1980); very fine-grained structures may be typical of greigite (= 'melnikovite' [Fe₃S₄] in

SETTING		NAME		REFERENCE
UNDERGROUND	PRIOR TO EXPOSURE	COVELLITE ¹	CuS	De Wijkersloot, 1948
		CERUSSITE	PbCO ₃	De Wijkersloot, 1948
		MALACHITE	Cu ₂ CO ₃ (OH) ₂	De Wijkersloot, 1948
		ANNABERGITE ?	Ni ₃ (AsO ₄) ₂ ·8H ₂ O	(author's data)
		"APATITE"	Ca ₅ (PO ₄) ₃ (F, OH, Cl)	Kimpe, 1973
	AFTER EXPOSURE	GALENITE ?	PbS	Driessen, 1962
		ARAGONITE ?	CaCO ₃	Driessen, 1962
		"LIMONITE"	FeOOH	Driessen, 1962
		EPSOMITE	MgSO ₄ ·7H ₂ O	Geol. Survey coll.
		"LIMONITE"	FeOOH	(author's data)
SURFACE	DUMPS	THENARDITE	Na ₂ SO ₄	this paper
		JAROSITE	KFe ₃ (SO ₄) ₂ (OH) ₆	this paper
		GYPSUM	CaSO ₄ ·2H ₂ O	this paper
		MIRABILITE	Na ₂ SO ₄ ·10H ₂ O	(author's data)

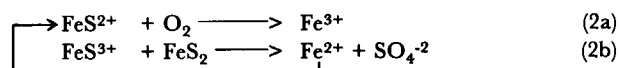
Table 1. A — Malachite has, apart from de Wijkerslooth's (1948) record from the Julia state colliery, been encountered regularly at the Hendrik/Emma dump as crusts on chalcopyrite crystals. B — Recent mineral genesis was recorded by Driessen (1962) from an abandoned gallery in the Oranje Nassau colliery. This gallery, excavated during 1909-1910, was re-opened for coal petrographic studies, after which large amounts of calcareous sediments were noted (aragonite ?). Mineralogical and chemical data are not provided. C — Mineral genesis starting when the rock dump comes into contact with the open air, may be referred to this group. These minerals are described in the present paper. Because of the dominance of pyrite the occurrence of sulphates was to be expected. Locally there are concentrations of thenardite and gypsum. Hydrate iron sulphate occurs here as a jarosite-type mineral (see below). N.B.: Kimpe (1963) described sulphur (α-S) from the former Staatsmijn Julia at Eygelshoven. This element had formed through a reduction of mining water with an extremely high H₂S content; it was found as bright yellow crusts on the walls of galleries.

Russian and older literature). The outer surface of such specimens often shows subhedral crystals (see Pl. 2, Fig. 2), the delimitations of crystals consisting of faces with low indices (see *e.g.* Leggewie & Jongmans, 1931); {100} (occasionally with minor {111} and {210}, in combination with {100}) have been recognised. In addition, pyrite manifests itself in crusts and fissure fills in brecciated rock zones.

Pyrite is a mineral which oxidises easily under aerobic conditions:



A large amount of pyrite occurring in the Carboniferous rocks of the Brunssum dump has disintegrated mechanically and, subsequently, chemically. This may have initiated sulphate genesis (speed-controlling reactions according to Singer & Stumm, 1970):



Only a small part of the pyrite has not disintegrated, comprising mainly subhedral and euhedral crystals. The sensitivity for redox reactions is much less in regular crystal lattices than in lattices with failures and inclusions (Silverman & Ehrlich, 1964). Adhesive forces amongst the elementary parts of crystal surfaces of a perfect structure are strongest (Kleber, 1990), which is why mechanical disintegration will trigger dissolution. Mechanically eroded pyrite concretions found at the dump often show jarosite crusts on cleavage surfaces (Pl. 2, Fig. 3). The oxidation rate is primarily dependent of the presence or absence of ferric iron which attacks pyrite. Oxidation under the influence of O_2 is a slow process (Stumm-Zollinger, 1972), but chemo-autotrophic bacteria may accelerate it.

Pyrite concretions are found in the oldest sites of the dump as well as in material dumped in the latest phase of production of the Emma colliery. Disintegrated pyrite and Fe sulphates occur commonly, although a larger concentration of Fe sulphates in group C is found (Fig. 2). This occurrence clearly shows that oxygen is a very important factor in pyrite oxidation here. Which factor dominates during oxidation in a natural environment is difficult to determine, because various oxidants may be present simultaneously (Silverman & Ehrlich, 1964). The group C dump is situated at the base of the waste dump, and belongs to the oldest layer in the area

investigated. The dump material is of the 'schachtsteen' type (Ritt, 1977), which is a very coarse type of debris coming directly from the exploitation front (Pl. 1, Fig. 3). Through a combination of low density, low dust/grit amounts and timber present, these layers include a considerable amount of oxygen, which is used up freely during oxidation. The jarosite/gypsum ratio is balanced quantitatively, both sulphates co-occur. Pyrite oxidation causes acidification of the surrounding environment and optimises also the ecological setting of the Fe oxidising bacteria of the *Ferrobacillus/Thiobacillus* group; they exist however in a relatively small area with regard to the acidity of their environment (pH 2.5-4.5) (Schnaitman *et al.*, 1969). The upper limit is at pH 6.5, above which cells of chemoautotroph micro-organisms cannot survive. Oxidation velocity under the influence of pH has been the subject of several studies (see *e.g.* Schnaitman *et al.*, 1969; Singer & Stumm, 1970). Without doubt, there exists a relationship between the capacities of the Fe oxidising bacteria and pH values. Schnaitman *et al.*'s (1969) results show that at pH 2.4-3.6 the oxidation is fastest (*Ferrobacillus ferrooxydans*, glycine- SO_4^{-2} and β -alanine- SO_4^{-2} buffers). pH values measured at the Brunssum dump are 3.8 at the most acidic spots and not extremely low (Fig. 3). pH measurements at freshly excavated parts have been performed to 2 metres below surface, where the rocks have been subject to a relatively strong mechanical erosion. From the data presented by Schnaitman *et al.* (1969), it is apparent that the optimum rate has not been reached here (yet).

SULPHATE MINERALOGY

— *Thenardite*, orthorhombic (Na_2SO_4)

Thenardite is a sulphate mineral frequently occurring during pyrite oxidation. The often extremely high Na concentrations in Carboniferous water (Driessen, 1962) are the reason for the common occurrence of this mineral type at the erosional surfaces of waste dumps of collieries. They cause great horticultural problems (Dijkstra, 1962; Wiggering, 1986; Schneider, 1990). The crystal structure of thenardite has been studied in a natural setting by Hawthorne & Ferguson (1975).

The crystallised Na sulphate is easily visible at erosional surfaces of the dump, as is jarosite. Thenardite occurs as clear white crusts on dark Carboniferous shales (Pl. 2, Figs 6, 7). Since water can percolate freely through the dump and at the

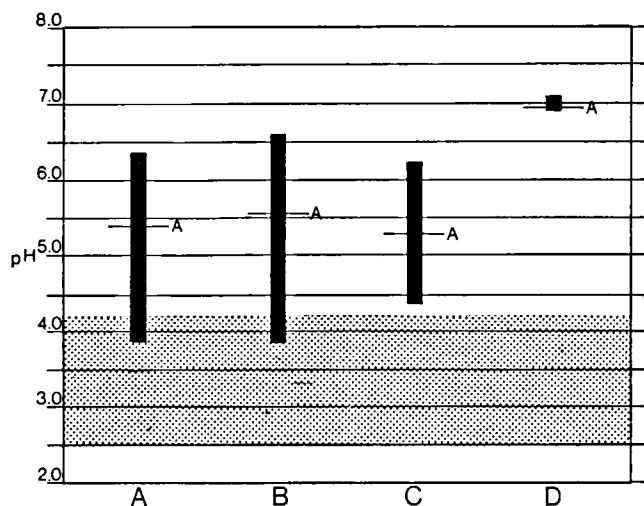


Fig. 3. Graphic presentation of the results of a few pH-measurements. Groups A, B and C each represent a number of closely-spaced sampling spots (see Fig. 2); the samples were taken of visually recognisable jarosite/gypsum concentrations in the field. This resulted in a mean pH value of 5.5 (mean value of each group separately indicated as "A").

For ease of reference a number of measurements carried out on jarosite/gypsum-free spots is indicated as group D (measure spots 23-29 in Fig. 2). Each of the last points consists of five sampling spots, situated at different vertical positions in the excavated section and distributed between the base and the top of the dump. The pH at the jarosite/gypsum-free places is very constant with fluctuations of some tens of entities.

The shaded area is the milieu in which the growth and oxidising capacity of Fe-oxidising bacteria is most prolific (see text for details).

base there is no large water emission, such crusts are only visible at a few places. The largest concentrations are present on spots indicated in Fig. 2 ('channel'), directly adjacent to the highest part of the dump. Here are present several gullies in which the percolating water is trapped. At the rims of these gullies thenardite crusts can be seen. On other spots on the faces smaller and less thick concentrations may be seen.

An X-ray analysis has been performed by Prof. Dr P.C. Zwaan (National Natural History Museum, Leiden) on material coming from the spot indicated by 'channel' in Fig. 2. The film (Debye-Scherrer, Fe tube, diameter 115 mm) is housed at the National Natural History Museum under registration number NNHM 202 979. A survey of the most intensive reflections is tabulated in Table 2, together with the values of synthetic Na₂SO₄ measured by Swanson & Fuyat (1953). During the field work it

appeared that part of the white minerals collected had a typical ice-like appearance; this became even clearer under the microscope. Very probably this concerns mirabilite (monoclinic NaSO₄·10H₂O), which is unstable within a dry atmosphere and under relatively high temperatures (>32.38°C, but because of mixing with strange ions markedly lower).

Brunssum thenardite			synthetic thenardite	
d	I	hkl	d	I
4.65	8	111	4.66	7
3.83	4	022	3.84	2
3.18	6	131	3.18	5
3.07	6	040	3.07	5
2.76	10	113	2.78	10
2.62	6	220	2.64	5
2.32	6	222	2.33	2
1.858	7	153	1.85	6
1.672	5	260	1.66	8
1.548	5	333	1.54	<1
1.426	5	206	1.42	5
1.290	4	246	1.29	6
1.275	4	066	1.27	5
1.073	4	119		
1.059	4	533		

Table 2. Comparison of the most intensive reflections of an X-ray analysis of Brunssum thenardite with the values of synthetic Na₂SO₄, as measured by Swanson & Fuyat (1953).

Under the microscope, it became apparent that the collected 'mirabilite', which was stored in a warmer and drier environment, turned rapidly into white powdery thenardite. The alleged mirabilite occurs exclusively at the rims of the gullies. Thenardite occurs, in addition to the gullies, also on the exposed surfaces of the waste dump. Probably the development of these two mineral species takes place independently for a large part. Thenardite genesis may be the result of dehydration of mirabilite (Ericksen *et al.*, 1970); the lack of any trace of mirabilite on the weathering surfaces (during extended periods of observation under all weather conditions), indicates that thenardite may develop also without the intermediate stage as the first sulphate on such surfaces.

— *Jarosite*, trigonal $XFe_3^{3+}(SO_4)_2(OH)_6$

Several mineral species with jarosite-type structure and composition are grouped in an alunite group with common molecular formula $XY_3(SO_4)_2(OH)_6$, in which the X stands for either Na, K, H_3O , Pb or a few other cations, and Y may represent Al (alunite series) or Fe (jarosite series) (Botinelly, 1976).

In a natural environment, jarosite-type structured minerals often form admixtures with contamination of limonite-like substances. Non-contaminated representatives are rare, which explains why crystal chemical and structural studies should be carried out with the utmost caution. Jarosites are typical of settings with a high redox potential, low temperatures and acid milieu. The commonest naturally occurring jarosite types as oxidation products of iron sulfides are hydroniumjarosite ('karphosiderite' in the older literature; $X = H_3O$), natrojarosite ($X = Na$) and jarosite s. str. ($X = K$). The crystal structure has been described by Hendricks (1937). Unit cell parameters have been determined by means of various XRD techniques by Botinelly (1976). Jarosite mineralisation mostly occurs in the form of very fine-grained masses, the extremely small crystals being pseudocubic or rhombohedral (hydronium-jarosite). Jarosite crystals visible to the naked eye could not be found at the Brunssum dump, where it occurs solely as extremely fine-grained masses. It occurs as spherical aggregates, which grow more or less close together (Pl. 2, Figs 4, 5). The density may be so high as to form connected crusts. The colour of pure jarosite is light yellowish, corresponding to Munsell 5Y 8/5 (Goddard *et al.*, 1984). Inclusions cause darker, brownish red hues.

Iron sulfide types are very close with regard to composition, which is why Dutrizac & Kaiman (1976)'s combination of chemical and X-ray analyses was followed. Both types of analysis were performed at the laboratories of the N.V. Koninklijke Sphinx (Maastricht): under a binocular microscope as pure as possible (= the lightest yellowish) piece of jarosite was removed from sample no. 616 of the author's collection. The results of chemical analysis are shown in Table 3; CaO and MgO have not been determined. It may be assumed that contamination of CaO occurs as a result of Ca ions becoming liberated from surrounding black shales upon S oxidation. The CaO complex may take the place of SO_4 in the jarosite lattice. From the analysis it is apparent that a comparatively large amount

Brunssum jarosite			Basic-ferric sulphate	
d	I	hkl	d	I
5.93	20	101		
5.67	14	003	5.68	36
5.08	60	012		
3.66	18	110	3.67	9
3.12	70	021	3.13	97
3.07	100	113	3.08	100
2.83	12	006	2.83	18
2.54	14	024	2.54	18
2.27	20	107	2.27	40
1.98	25	303	1.98	38
1.83	25	220	1.83	36

Table 3. Results of a chemical analysis of Brunssum jarosite, as compared with values for basic ferric sulphate (Mumme & Scott, 1966).

of SiO_2 and Al_2O_3 were present in the sample (? illite). Heat loss has been determined at $450^\circ C$ and $1,000^\circ C$, in the first instance loss amounted to 15%. By means of DTA techniques it was shown that at $470^\circ C$ an endothermic reaction took place, triggered by the loss of OH, simultaneously leading to the collapse of the jarosite structure (Kulp & Adler, 1950). Exothermic curves are in DTA measurements of sulphates very weak and originate primarily from dehydration (Smykatz-Kloss, 1974). The X-ray analysis was performed using a Philips PW 1410 ($CuK\alpha$ radiation): the material studied originated from the same sample as used for a chemical analysis. The diffractogram is illustrated in Fig. 4, compared with the X-ray diffractogram of basic ferric sulphate (Mumme & Scott, 1966). Mumme and Scott's synthesised basic ferric sulphate [$3Fe_2O_3 \cdot 4SO_3 \cdot 9H_2O$] came into existence through hydrolysis of a ferri-sulphate solution at a temperature of $140^\circ C$. In the diffractograms, the intensive double reflection at 2θ ca 30 is characteristic. These reflections represent d (cal.) 3.131, 3.087, hkl 012 and 113, respectively. Such high intensity peaks occur with most end members of the jarosite series (Dutrizac & Kaiman, 1976). X-ray analysis also revealed the quartz contamination as a strong reflection at 2θ 27 (d 3.24). The other reflections show the typical picture of jarosite structure; most have a relatively high d-value.

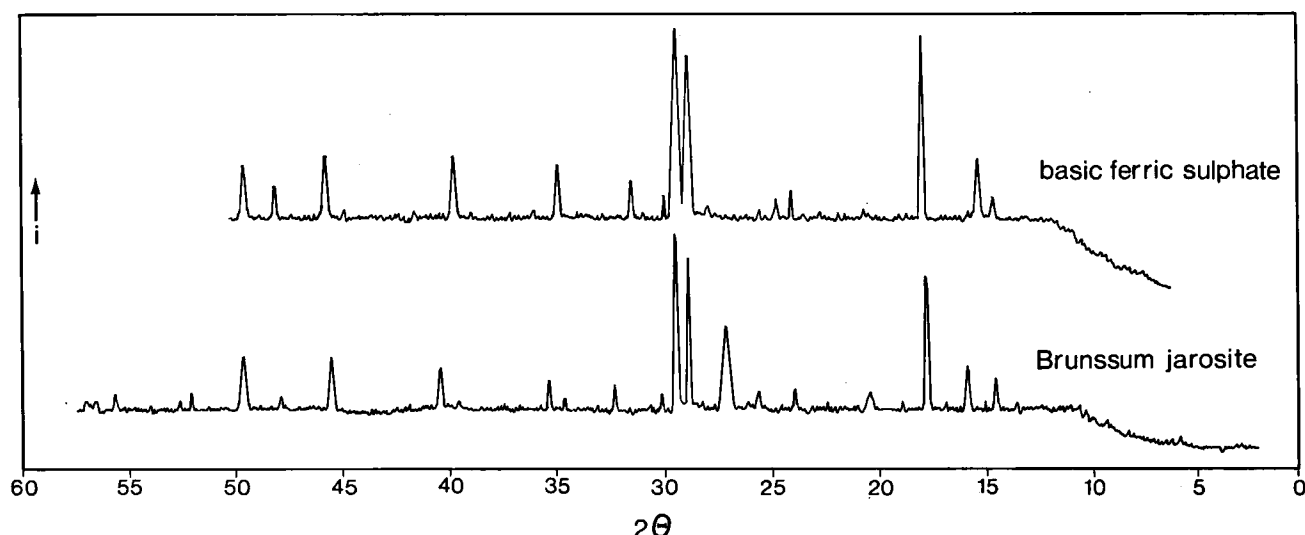


Fig. 4. Brunssum jarosite diffractogram compared with X-ray diffractogram of basic ferric sulphate (Mumme & Scott, 1966).

As mentioned above, most naturally occurring jarosites are admixtures of jarosite, natrojarosite and hydroniumjarosite, which holds true also for the Brunssum sample. A comparison with JCPD maps of the most dominant as well as weak peaks in the diffractogram, shows that these correspond closely to data presented for jarosite (Table 4).

— *Gypsum*, trigonal $\text{Ca}(\text{SO}_4) \cdot 2\text{H}_2\text{O}$

The hydrate calcium sulphate gypsum is the commonest sulphate species having been described in numerous mineralogical papers. The crystal structure has been determined by Wooster (1936) by

means of Fourier XRD, and has on numerous occasions been revised (see e.g. Cole & Lancucki, 1972, 1973, 1974). A physical characteristic is the remarkably good cleavage along (010), and translations in this direction being common, gypsum may follow movements during and subsequent to crystallisation. The speed of crystallisation may be extremely high under natural conditions (Zedniček, 1954).

Gypsum genesis, as a result of pyrite oxidation, is a commonly occurring phenomenon. Acids liberated during oxidation may corrode carbonates present, and initiate gypsum genesis under favourable physicochemical conditions. Such a process may account for the presence of gypsum at the Brunssum dump. That gypsum has appeared early may be seen in places where jarosite and gypsum co-occur; gypsum usually grows at the expense of jarosite.

Gypsum morphology is largely dependent of environmental parameters:

1 - extremely flat crystals occur on splitting planes of shales: room to grow was very limited for this type of crystals. The crystal position with regard to the overgrowth of shales is invariably parallel to (010), and development in the direction of the crystallographic B-axis has virtually not been accomplished, when compared to other directions (Pl. 3, Figs 1-4). In general, growth of the {010} pinacoid is slower than of other faces, which has also been noted in synthetic crystals (Eddinger, 1973). The length ratios of crystallographic axes show a wide

Wth %	1	freq. ox.	2	3
SiO ₂	11.6	0.204	0.37	
Al ₂ O ₃	8.0	0.082	1.98	
Fe ₂ O ₃	16.6	0.109	48.90	49.25
K ₂ O	2.2	0.024	0.52	5.90
Na ₂ O	3.7	0.063	0.43	0.80
SO ₄	26.5	0.292	32.71	31.76
H ₂ O	1)	1.503	15.09	11.35
Total	94.2		100.00	99.06

1) Heat loss: 450°C = 15.1
1000°C → 10.5

1) Brunssum, this paper. Analysed by Ir V. Scholtijs.
2) Walbrzych, Poland (Kubisz, 1961)
3) Jaroso, Spain (Hintze, 1930)

Table 4. Comparison of Brunssum jarosite with literature data.

range of variation; although the thickness to [010] never exceeds c 1 mm. Sizes in the other directions vary from a few to 50 mm (Fig. 5). In many crystals, {010} has developed; the limited room has obviously not always been used up fully. The slow growth of {010} is present here too. Twinning is seen in many crystals as contact twins with contact plane (100) (Pl. 3, Fig. 1), some concentrations of crystals being composed exclusively of such 'swallow tail twins'. Other faces are very small and consist of {120}, {011} and {111}. The crystals follow exactly the relief of the shales, such as the prominent undulations of the common plant fossil *Sigillaria* spp., an arborescent lycophte;

2 - aggregates occurring in the outer zones of siderite concretions: these are spherical. The nucleus of such aggregates consists of opaque white to yellowish crumbly gypsum. Crystals radiating from this point are transparent white. Individual crystals are often so closely spaced that spherical aggregates occur. Only {010} may be seen on the crystals. The aggregate diameter amounts to c 0.5 mm;

3 - free prismatic crystals found amongst rock debris commonly associated with jarosite: the most room for growth of crystals was found amongst the debris of the earliest dumping. At these places gypsum and jarosite co-occur, and both species are present in each of the samples collected. Parageneses of these minerals have been described in the literature by *e.g.* Ljunggren (1955) and van Tassel (1958).

There is a wide range of variation as far as size of the crystal faces is concerned. Generally, it may be observed that {010} predominates, being prismatic along [100]. The length in this direction varies between 0.1 and 2.5 mm. The number of face combinations observed in gypsum crystals is minimal; {120}, {010} and {011}. Twinning has not been found. The grouping of crystals is often chaotic in nature, and to a lesser degree radially arranged. Transparency is also very variable. It is a well-known fact that gypsum may easily incorporate large quantities of contaminating material in its lattice. In otherwise transparent crystals, carbonaceous material is seen distributed at random (Pl. 3, Fig. 5).

DISCUSSION

On the +70 year old waste dump of the former collieries Emma and Hendrik at Brunssum, oxidation of iron sulfide minerals takes place on a large

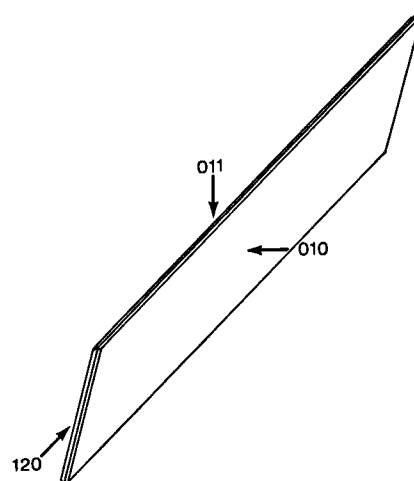


Fig. 5. Idealised crystal shape of gypsum, as it is found on the bedding planes of Carboniferous shales. Compare Pl. 3, Figs 1, 2.

scale, leading to the genesis of SO_4^{-4} and acidification to an average of pH 5.5. Currently, the above-mentioned sulphates become liberated in large quantities, which in part reach ground water. A discussion of the environmental aspects of this process is deferred to another occasion. For a general discussion of environmental-geotechnical aspects of pyrite oxidation the reader is referred to a number of German publications (Siebert & Werner, 1969; Döngelhoff *et al.*, 1983 and Schneider, 1990) (see Fig. 3).

Thenardite occurs here as a result of removal of Na ions, a process still taking place after 70 years. This mineral crystallises together with mirabilite (?) mainly at the rims of some gullies at the northern side of the dump, in which water that has percolated through the dump is trapped. Thenardite occurs as crusts of irregular shape; idiomorph crystals do not occur. As far as could be determined from the available literature, this is the first record of thenardite for The Netherlands.

The process of exogenetic pyrite oxidation in black Carboniferous shales is nearly always accompanied by jarosite and gypsum genesis (Kubisz, 1961; Grünhagen, 1982; Wiggering, 1986; Joachim, 1991). At the Brunssum dump pyrite oxidation is witnessed by the occurrence of gypsum and bright yellow jarosite stains on weathering surfaces. Finely distributed pyrite as well as larger concretions trigger sulphate genesis here. Jarosite occurs in superficial layers as well as in deeper uneroded parts of the dump. Gypsum has in most cases crystallised well as

idiomorph crystals, crystal shape naturally being dependent of the available room during growth.

The mineral association found here is typical of the oxidising, acid environment of pyrite-bearing shales dumped in an equable/continental climate. Current re-structuring and excavation of the Brunssum dump will make additional mineralogical observations impossible within the (near) future.

ACKNOWLEDGEMENTS

Much appreciated technical support during the present study was offered by Ir V. Scholtjjs, Laboratory of N.V. Koninklijke Sphinx (Maastricht). Prof. Dr P.C. Zwaan (National Natural History Museum, Leiden) prepared and interpreted an XRD analysis of thenardite, for which I am grateful. Prof. Dr E. Zodrow (University College of Cape Breton, Nova Scotia, Canada) supplied many items of literature and suggested improvements to the manuscript. The assistance of Dr A. Germann (RWTH Aachen), G. Geraeds (Roermond), S. Schneider (GLA Krefeld) and Prof. emer. Dr R. van Tassel (Berchem) is gratefully acknowledged.

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PLATE 1

- Fig. 1. View of sampling spot 28. Dumping of late production phase of colliery Staatsmijn Emma. (Photo taken January 1992).
- Fig. 2. View of spot B. Dump increasing from left to right. (Photo taken December 1991).
- Fig. 3. The very loose dump of group C with numerous fragments of mining timber. (Photo taken December 1991, width of picture \approx 0.8 m).
- Fig. 4. Close dump with high dust/grit content, some metres above and east of group C. (Photo taken January 1992, width of picture \approx 0.8 m).

PLATE 1



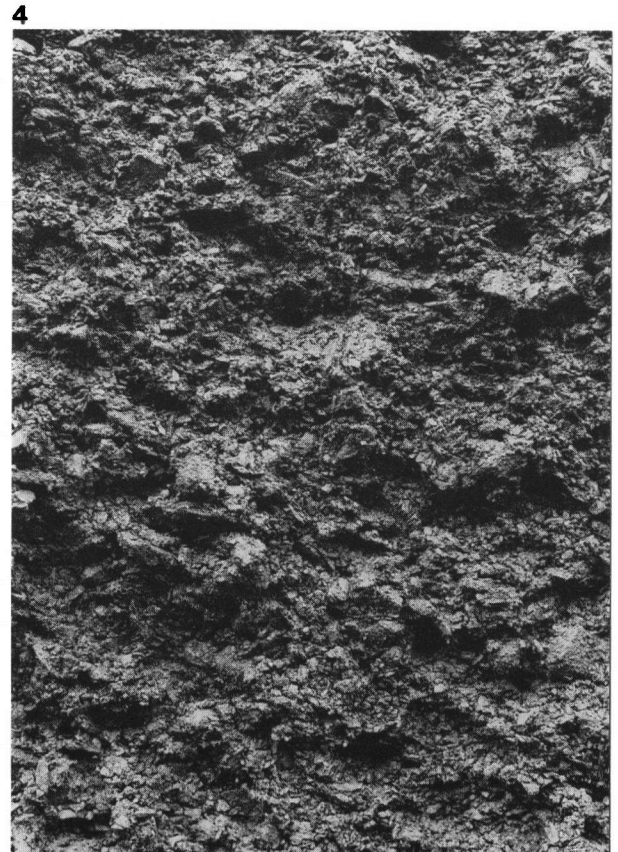
1



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3



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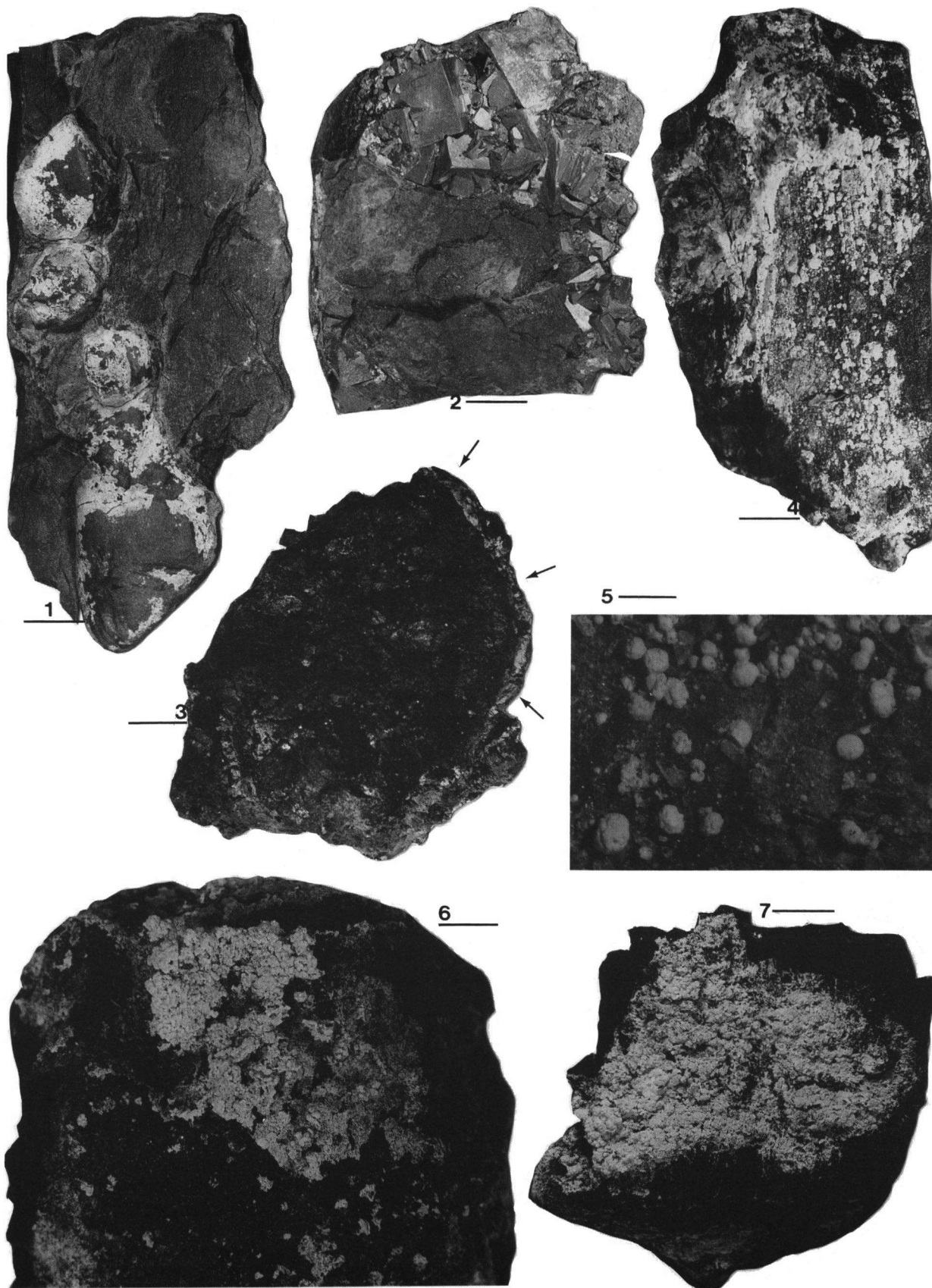
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PLATE 2

All specimens from Emma/Hendrik waste dump, Brunssum.

- Fig. 1. Siderite concretions in shale. Bongaerts Collection, no. 739. Scale bar equals 10 mm.
- Fig. 2. Pyrite. Bongaerts Collection, no. 299. Scale bar equals 10 mm.
- Fig. 3. Pyrite, almost entirely disintegrated, with jarosite encrustation (arrows) on external surfaces. Bongaerts Collection, no. 327. Scale bar equals 10 mm.
- Fig. 4. Jarosite (white spots in photograph). Bongaerts Collection, no. 328-1. Scale bar equals 10 mm.
- Fig. 5. Jarosite, spherical aggregates. Bongaerts Collection, no. 328-2. Scale bar equals 1 mm.
- Fig. 6. Thenardite. Bongaerts Collection, no. 358-1. Scale bar equals 10 mm.
- Fig. 7. Thenardite. Bongaerts Collection, no. 358-2. Scale bar equals 10 mm.

PLATE 2



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Manuscript received 12 June 1992, revised version accepted 28 May 1993.

PLATE 3

All specimens from Emma/Hendrik waste dump, Brunssum.

- Fig. 1. Gypsum. Bongaerts Collection, no. 162. Scale bar equals 0.5 mm. Radially arranged aggregate, principally consisting of swallow tail twins.
- Fig. 2. Gypsum. Bongaerts Collection, no. 1470. Scale bar equals 20 mm.
- Fig. 3. Gypsum. Bongaerts Collection, no. 208. Scale bar equals 0.5 mm. Cross polarised.
- Fig. 4. Gypsum. Bongaerts Collection, no. 208. Scale bar equals 10 mm. Extremely flattened, strongly coalesced crystals on sandstone-like shale.
- Fig. 5. Gypsum, Bongaerts Collection, unregistered. Scale bar equals 0.5 mm. Inclusions of carbonaceous material.

PLATE 3

