Recent secondary minerals in the Billingham anhydrite mine.

By L. R. Raymond, B.Sc.
Research Dept., Imperial Chemical Industries Ltd.,
Billingham-on-Tees, Durham.

[Taken as read, 2 April 1959.]

Summary. A number of secondary minerals have grown in recent years in a part of the Billingham anhydrite mine, by evaporation of water from the Upper Magnesian Limestone, and include some unusual species, the most interesting of which is thought to be *ilsemannite.*

THIS mine is located beneath Imperial Chemical Industries' factory site at Billingham, about 3 miles NE. of Stockton-on-Tees. The workings are in the Main Anhydrite, between 500 and 900 feet below sea-level. The anhydrite, which immediately overlies the Upper Magnesian Limestone, has been disturbed only slightly on a regional scale but locally strong disturbances have broken the gentle regional south-easterly dip. Some of these disturbances are in the form of asymmetrical synclines with one vertical limb. These synclines may cover an elliptical area over 300 yards long and 60 yards wide. Part of the steep limb of one such syncline was mined (see fig. 1) but was abandoned because the anhydrite became attenuated and water from the Upper Magnesian Limestone flooded the working. About two years after the working was abandoned, it was found that multicoloured efflorescences had grown in irregular scattered patches on part of the exposed limestone and anhydrite forming the walls and floor of the working. The efflorescences on the walls were mainly in the form of crusts or tufts of acicular growth, those on the floor coral-like and often very beautiful. The colours of the growths included light blue, vivid dark blue, green, yellow, orange, brown, white, and colourless. Specimens of each type were collected and examined microscopically, but with great difficulty as the crystals were usually only a few microns across. In view of this, X-ray and spectrographic examinations were also carried out on most of the material.

Dark blue efflorescence. This consisted of a hygroscopic crust of crystals which, when dried in a desiccator, gave a yellow powder with a green-blue surface layer. The latter contained halite, anisotropic crystals too small to identify, and blue material that picked up water too quickly for microscopical examination to be effective. X-ray examination indicated halite, epsomite, and an unidentified phase. The yellow powder contained a trace of normal halite with *n* 1·544 and some isotropic crystals with *n* 1·539±0·002. The latter phase was also identified as halite by X-ray examination. It should be noted here that several of the efflorescences contained isotropic crystals identified as halite by X-rays but with *n* persistently 1·539. The yellow powder also contained aggregates of exceedingly fine-grained anisotropic crystals that could not be identified, and rectangular prismatic crystals thought to be aphthitalite.

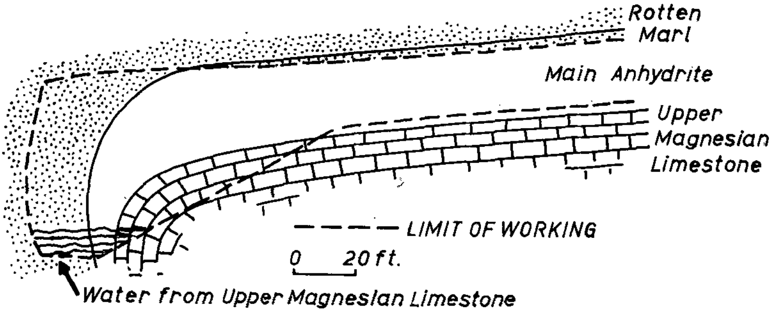

FIG. 1. Cross-section of part of a syncline, anhydrite mine, Billingham, Durham.

The above examinations did not explain the strong blue colour of the unaltered efflorescence, so it was decided to resort to chemical analysis. A sample was leached with water, and the resulting solution gently evaporated to dryness and analysed with the following result: MoO_3 6·4, SO_3 23·4, Na_2O 22·4, K_2O 0·2, CaO 0·5, MgO 1·4, $(Fe,Al)_2O_3$ 9·6, Cl′ 22·8, loss at 400° C. 18·6 %, total (less O = Cl 5·1) 100·2 %. The loss at 105° C. was only 4·3 %. The amount of molybdenum was remarkable and was clearly responsible for the bright blue colour. It remained in solution until evaporation was carried almost to complete dryness and was therefore exceedingly soluble.

The efflorescence was undoubtedly precipitated out of Upper Magnesian Limestone water which crept up and evaporated from the walls of the working. However, an analysis of the water revealed no molybdenum, neither did spectrographic examinations of the surrounding rocks. The water analysis suggested the following combinations: $CaCO_3$

100 p.p.m., $MgSO_4$ 2 580 p.p.m., $CaCl_2$ 14 740 p.p.m., $MgCl_2$ 6 650 p.p.m., and NaCl 84 240 p.p.m. For comparison, Sunderland Town water which is also obtained from the Magnesian Limestone contains the following suggested combinations: $CaCO_3$ 201 p.p.m., $MgSO_4$ 57 p.p.m., $CaCl_2$ 17 p.p.m., NaCl 38 p.p.m., and $MgCO_3$ 89 p.p.m.

Examination of the water-insoluble residue of the blue efflorescence revealed gypsum, talc, sulphur, abundant pyrite crystals (anhedral, botryoidal, cubes, octahedra, and rare pyritohedra), together with possible small amounts of arsenopyrite and molybdenite. Spectrographic examination of this material indicated Fe, Ca, S, Si, Mo, K, As, Zn, and Al.

Pale yellow efflorescence. This was all water-soluble and consisted mainly of halite (X-ray) with n 1·539±0·002. A small amount of a rectangular prismatic phase, with extinction inclined up to 40° and exhibiting lamellar twinning, was tentatively identified as tamarugite. A little tachhydrite was also thought to be present (the sample contained some hygroscopic phase).

White efflorescence. The major phase was isotropic and was identified by X-rays as halite, but with $n = 1{\cdot}539$. Some gypsum and a little sylvine were present. Spectrographic examination indicated traces of Cu, Al, Bi, and Sr, but no minerals containing any of these elements were identified. Some colourless to white curved bladed crystals about 1 cm. in length proved to be thenardite. When removed from the mine they broke down to a white powder, but still consisted of thenardite.

Brown efflorescence. This mainly consisted of gypsum, with a coating of rusty brown material identified as lepidocrocite. A little halite was also present.

Orange efflorescence. The major phase was halite in well-formed cubes, in needles, or as granules. A little gypsum was also present, and an unidentified extremely fine-grained yellow material. The spectrograph indicated Cl as a major element and Fe, Ca, and Na as minor elements. It seemed, therefore, that the yellow material was largely iron chloride.

Yellow efflorescence. Most of the material was present as laths and acicular crystals with indices between 1·602 and 1·698, and was almost certainly an iron sulphate of some kind (the spectrograph indicated strong Fe and S but X-ray analysis could not identify it). A little halite was also present.

An interesting efflorescence of trona is widespread on the rise side of the mine. It occurs as colourless needles and plates, growing on rusty rails, bolts, &c., but can never be found on wood or stone.

Conclusions.

Briefly, the mineralogy of the efflorescences was as follows: Proved present, halite, thenardite, gypsum, epsomite, talc, sylvine, pyrite, sulphur, lepidocrocite. Probably present, ilsemannite, tamarugite, tachhydrite, a ferric sulphate, ferric chloride. Possible or doubtful, aphthitalite, arsenopyrite, molybdenite. There was clearly no doubt that the efflorescences were very recent secondary growths that had been precipitated from Upper Magnesian Limestone water that had crept up the walls of the working and evaporated.

The most interesting feature of the investigation was the discovery of molybdenum. It was thought to be in the form of ilsemannite or molybdenum blue and was undoubtedly responsible for the blue coloration of the first efflorescence described, which, like the other efflorescences, was precipitated largely from limestone water. However, waters rich in calcium, such as the limestone water, should precipitate any molybdenum in the form of insoluble salts. If it is assumed that the ratio between molybdenum and the other dissolved substances in the limestone water should roughly correspond to the ratio of molybdenum to the other solids in the efflorescences, then approximately 0·7 % of molybdenum should have been present in the limestone water, but, in fact, none was detected (< 1 p.p.m.). It seemed impossible therefore that evaporation of this water could yield an efflorescence containing such a large amount of molybdenum. The wall rock behind the blue efflorescence was examined but it contained no molybdenum (it was thought that limestone water generally containing no molybdenum might have leached molybdenum out of localized areas of the wall rock as it seeped upwards).

Chrome molybdenum steel drilling bits are used in the mine and it was thought that a fragment of this material might have been the source of the molybdenum. However, this also appears to be unlikely in view of the distribution of the blue efflorescence and also the fact that no chromium was detected.

Such conflicting evidence obviously precludes the possibility of explaining how the ilsemannite was formed and the origin of the molybdenum can only be the subject of speculation.

Acknowledgements. Professor K. C. Dunham very kindly read the manuscript and his suggestions and encouragement are gratefully acknowledged. The assistance of my colleagues Dr. J. M. Skinner and Dr. T. T. Harding, who carried out respectively the chemical and X-ray analyses connected with this work, is also gratefully acknowledged.