Mineral Resources
Consultative Committee

Mineral Dossier No 8

Sulphur

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London
Her Majesty's Stationery Office
1974

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Preface

The Mineral Resources Consultative Committee consists of representatives of interested Government Departments, and specialist advisers. It was set up in 1967 to keep present and future requirements for minerals under review and to identify problems associated with the availability, exploitation and use of mineral resources, both inland and offshore, having regard to competing demands on land use and other relevant factors.

Widespread and increasing interest in the mineral resources of the United Kingdom has led the Committee to undertake the collation of the factual information at present available about those minerals (other than fossil fuels) which are now being worked or which might be worked in this country. The Committee has produced a series of dossiers, each of which was circulated in draft to the relevant sectors of the minerals industry. They bring together in a convenient form, in respect of each of the minerals, data which had previously been scattered and not always readily available. These dossiers are now being published for general information.

Acknowledgements

This dossier has been compiled with the assistance of the Department of Trade and Industry, the Department of the Environment and the Welsh Office. Within the Institute of Geological Sciences, particular thanks are due to Mr D Horne of the Mineral Statistics and Economics Unit of the Mineral Resources Division. The help of the following companies and associations, some of which commented extensively on drafts of the dossier, is also gratefully acknowledged; Albright and Wilson Limited, Berk Spencer Acids Limited, British Steel Corporation, British Sulphur Corporation Limited, British Titan Products Company Limited, Central Electricity Generating Board, Courtaulds Limited, Fisons Limited, Imperial Chemical Industries Limited, National Sulphuric Acid Association Limited, Simon-Carves Limited and United Sulphuric Acid Corporation Limited.

Metric units are employed throughout this document except where otherwise stated. In most cases this has necessitated the conversion of originally non-metric data. The units and conversion factors used are as follows:

millimetres (mm) = inches x 25.4
metres (m) = feet x 0.3048
kilometres (km) = miles x 1.609344
litres (l) = US gallons x 3.78533
cubic metres (m^3) = cubic feet x 0.028317
kilogrammes (kg) = pounds x 0.45359237
tonnes (1000 kg) = long tons x 1.01605

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Summary

Sulphur is an essential raw material with a very wide range of industrial uses. It is used chiefly in the manufacture of sulphuric acid and to a lesser degree in the rayon, pulp, dyestuffs, pharmaceutical and rubber industries. The three most important commercial sources are (1) the deposits which form the cap-rock of a number of salt domes in the USA and Mexico and the sedimentary deposits in south-eastern Poland; (2) 'sour' or sulphur-bearing natural gas in which hydrogen sulphide (H_2S) is a deleterious constituent; and (3) pyrites, chiefly in the form of iron pyrites or pyrite (FeS_2). Other important sources are base metal sulphide concentrates, notably of zinc, during the smelting of which sulphur dioxide (SO_2) is evolved; H_2S recovered from oil refinery gases; and the calcium sulphate mineral anhydrite ($CaSO_4$).

The United Kingdom is a major world producer of sulphuric acid but is deficient in naturally-occurring sources of sulphur which can be worked economically, with the notable exception of anhydrite, which has been mined on a larger scale in the United Kingdom than in any other country and in 1972 accounted for about 11 per cent of the sulphuric acid produced. Estimated production of anhydrite amounted to 778,000 tonnes in 1972, almost all of which was used for making sulphuric acid. It was produced by Albright and Wilson Limited at Sandwith, Cumberland, and by British Gypsum Limited at the Long Meg mine near Penrith, Cumberland. Anhydrite was also mined by Imperial Chemical Industries Limited at Billingham, Co Durham, until August, 1971. The output has been consumed by the producing companies with the exception of anhydrite produced at Long Meg which was transported by rail to a sulphuric acid plant at Widnes in Lancashire until the plant closed in March, 1973. Other commercial sources of sulphur in the United Kingdom are spent oxide, SO_2 gases obtained from zinc smelting, and sulphur recovered at oil refineries. Together with anhydrite, these sources accounted for about one-fifth of total annual sulphur requirements, which were estimated to have been about 1.3 million tonnes in 1972. Domestic demand is therefore met largely by imports, chiefly of crude sulphur from France, Poland, Mexico and Canada, and of pyrites principally from Cyprus. Imports of crude sulphur and pyrites in 1972 were valued at nearly £11 million.

Large quantities of sulphur or sulphur compounds are also potentially recoverable from industrial waste (flue) gases and residual fuel oil. Although processes for the reduction of the SO_2 content of industrial waste gases to permissible limits have reached large-scale operation in the United Kingdom, they do not permit the economic recovery of sulphur. There is also growing interest in desulphurising fuel oil, but sulphur is not recovered from this source in the United Kingdom at present.

World production of sulphur and sulphur equivalent amounted to some 45.5 million tonnes in 1972 compared with about 42 million tonnes in 1970, when for the first time output of recovered sulphur (chiefly that derived from natural gas processing) exceeded production from Frasch and other primary sources. Most of the production came from the USA, Canada, the USSR, Poland, Mexico and France, the USA having dominated world production and trade for many years until 1968, when Canada became the principal sulphur-exporting country. The USA, Canada, Poland and France account for most of the world crude sulphur exports, supplying about 7.7 million tonnes in 1971, largely to markets in western Europe. World consumption of sulphur in all forms reached 31.8 million tonnes in 1972.

World resources of sulphur are extremely large and are believed to be sufficient to meet anticipated demand for many years. Historically the demand for elemental sulphur has grown at the rate of 4 to 5 per cent per annum but may rise above this level in the next few years. The demand is closely linked with that for phosphatic fertilisers, the largest single outlet for sulphuric acid, the slowing down in the sales of which as well as the introduction of new sources of supply of sulphur, led to an excess of supply in 1968 and a subsequent marked fall in sulphur prices. Since the Second World War periodic shortages of crude sulphur and accompanying high prices have prompted several countries to consider the use of raw materials other than crude sulphur and pyrites, particularly those available domestically. However, these sources are no longer economically attractive, except in special circumstances.

Definition and mode of occurrence

Sulphur has been known and used since earliest times, the name being derived from the Latin word for *brimstone* (burning stone). It is widely distributed in nature, occurring both in the free state and in direct combination with many other elements, notably as metal sulphides, hydrogen sulphide gas (H_2S) and calcium sulphate minerals. Sulphur combines with all metals, except gold. It also occurs in economically recoverable quantities in various industrial waste materials. Naturally occurring *elemental sulphur* is called *native sulphur.* It is a brittle, soft, crystalline mineral, bright yellow in colour, although earthy varieties may be orange, brown or grey. There is a relatively large number of allotropic forms of the element, of which the so-called 'rhombic' sulphur is the most stable form at ordinary temperature, occurring usually as simple pyramidal crystals. This sulphur has a specific gravity of 2.07 and melts at 112.8°C becoming a straw yellow, transparent liquid. With rising temperature, the colour of the sulphur darkens, until at the boiling point (444°C) it is nearly black. Elemental sulphur is inflammable, tasteless and odourless, insoluble in water but highly soluble in carbon disulphide and a poor conductor of both heat and electricity. On Mohs' scale its hardness ranges from 1.5 to 2.5. *Crude sulphur* or *brimstone* is elemental sulphur that is 99.0 to 99.9 per cent pure and is free from such impurities as arsenic, selenium and tellurium. *Recovered sulphur* is a term normally restricted to elemental sulphur produced either from hydrogen sulphide present in natural gas and oil refinery gases or derived from residual fuel oils. Sulphur is released as sulphur dioxide during the smelting of iron and base metal sulphides, the combustion of many fuels, and the calcination of calcium sulphate minerals.

By far the most important deposits of native sulphur occur as crystal aggregates, veinlets and disseminated particles in limestone and gypsum which, together with anhydrite, form the cap-rock of many salt domes scattered along the Gulf of Mexico from Louisiana and Texas to southern Mexico. The crude sulphur produced from these salt dome deposits is often known as *Frasch sulphur*, named after Herman Frasch who developed in the USA the process by which this sulphur is mined. The deposits lie at depths of between 150 and 760m, the thickness, configuration and sulphur content of the cap-rock varying considerably. A typical commercial deposit may have a sulphur-bearing zone up to 30m thick containing 20 to 40 per cent sulphur. Although over 400 salt domes have been discovered in the Mexican Gulf area, only some 32 domes have contained sufficient sulphur to warrant commercial development since production first began in Louisiana in 1894.

Similar deposits are worked chiefly in Poland, the USSR, Iraq, and in the USA in western Texas, in which sulphur occurs in veins, thin beds and as linings to cavities in limestone and gypsum, as well as lenses and nodules in gypsum and bituminous shales, but is not associated with salt domes. The grade of the rock mined generally ranges from 12 to 30 per cent sulphur, but locally pockets with 80 to 90 per cent may be present. In terms of supplies to world markets the most important of these sedimentary deposits was discovered in south-eastern Poland near Tarnobrzeg in 1952 in rocks of Miocene age, and subsequently found to cover an area of some 30 sq km. Two opencast mines have been opened up, exports beginning in 1961, the year after the Piaseczno mine became operational. This mine was closed in 1972 in favour of the Machow mine which works a bed averaging 10m in thickness and containing 27 per cent sulphur at a depth of 60m or more. Deposits are also worked by methods similar to Frasch mining at the Jeziorko mine; the bed is about 10m thick and lies at a depth of about 120m, containing an average of 25 per cent sulphur. It was reported early in 1972 that this mine provides nearly 50 per cent of total Polish sulphur production. The Grzybow mine works a bed averaging 15m in thickness at a depth of 180m and containing about 21 per cent sulphur. Numerous deposits containing up to 26 per cent sulphur have been worked in Sicily for many years and supplied virtually all the world's sulphur requirements during the early part of the 19th century. The sulphur occurs as incrustations, small pockets or thin beds in limestone of Miocene age.

Native sulphur is also found in most volcanic regions of the world, particularly in the Andes Mountains of South America and in Japan. Although total reserves are substantial, individual deposits are generally small and are mined only to a limited extent. The most important occur in Chile where some deposits contain 45 to 95 per cent sulphur. In Japan impregnations and replacements with 35 to 40 per cent sulphur have been extensively worked.

Recovered sulphur is obtained chiefly from hydrogen sulphide gases associated with natural gas, commonly referred to as 'sour' gas. One of the largest sour gas fields was discovered as a result of a geophysical survey carried out during the Second World War at Lacq in south-western France about 160 km south of Bordeaux. Gas is produced from an anticlinal reservoir of fractured limestones of Jurassic age at depths of 3,450 to 4,950m. The gas produced contains 74.6 per cent hydrocarbons, 15.2 per cent H_2S and 10.2 per cent nitrogen and carbon dioxide. The very large natural gas reservoirs in Canada lie in the Western Canadian sedimentary basin, notably in stratigraphical traps in the Rocky Mountain Foothills and the Alberta Plains. Carbonate rocks of Devonian and Lower Carboniferous age are the principal reservoirs, depths to the top of the productive formations frequently exceeding 1,500m. Most of the producing gas fields contain up to 20 per cent H_2S, but locally gas with 53 per cent H_2S is processed. As much as 87 per cent H_2S has been reported to occur in natural gas from the Panther River area approximately 110 km north-west of Calgary. The natural gas found to date in the United Kingdom sector of the North Sea has a very low sulphur content.

Pyrites is a general trade name for pyrite or iron pyrites (FeS_2), the less stable form marcasite, and pyrrhotite (Fe_nS_{n+1}). Iron pyrites is one of the most abundant of all sulphide minerals, occurring in lenses, veins and disseminated crystals. It commonly occurs as brassy-yellow lustrous cubes and cubic combinations, showing well-marked striations on the cubic faces parallel to alternate pairs of edges. When pure the mineral contains 53.4 per cent sulphur and 46.6 per cent iron; as mined, pyrites usually contains 30 to 50 per cent sulphur and small amounts of other elements, including arsenic, copper, gold, cobalt, nickel, zinc and tin. Among the largest commercial deposits are those situated within a belt extending from the province of Seville in southern Spain westwards into Portugal. The orebodies are usually large lenses which lie at the contact between slates and intrusive porphyritic igneous rocks. At the Rio Tinto mines in Huelva Province, for example, one of the lenses is more than 1½ km long and in places over 240m in width, the massive ore averaging about 48 per cent sulphur, with minor amounts of copper, lead and zinc. Iron pyrites is commonly present in coal, generally in a finely divided form, and in clays and shales, usually as disseminated crystals or as concretionary nodules.

Anhydrite ($CaSO_4$) and *gypsum* ($CaSO_4.2H_2O$) normally occur as stratified deposits of variable thickness interbedded with limestone, dolomite, shale or clay and are widely distributed throughout the world. Pure anhydrite contains the equivalent of 23.5 per cent sulphur. Usually it is massive, crystalline and white or grey in colour and as mined contains at least 85 per cent $CaSO_4$. Beds ranging from 2 to 8 m in thickness are worked commercially. Together with gypsum and limestone, anhydrite forms the cap-rock of many salt domes usually at depths of between 150 and 600m. Gypsum, when pure, is colourless to white, but commercial deposits are usually grey, brown, red or pink in colour, depending on the impurities present. Anhydrite and gypsum are among the first minerals to be precipitated from evaporating sea-water brines.

Sulphur is also recovered from sulphur-rich crude oils, oil shales and tar sands, while in some countries use is made of acid sludge obtained in oil refining by treating various petroleum fractions with concentrated sulphuric acid, phosphogypsum formed during phosphoric acid manufacture, ferrous sulphate produced at steel works when steel is immersed or 'pickled' in a bath of dilute sulphuric acid to remove surface scales, and spent oxide which is obtained when coal gas and coke-oven gas are purified with iron oxide. Ferrous sulphate is present also in the effluent discharged from titanium dioxide plants.

Resources

Anhydrite is the only known naturally occurring source of sulphur in the United Kingdom which is worked on a commercial scale. It has been used for many years for the manufacture of sulphuric acid and was also used in the production of ammonium sulphate fertiliser until April, 1971. There are also very large reserves of gypsum which, together with pyrites and such secondary sources as industrial waste gases, fuel oils, phosphogypsum and oil shale, are possible future sources of sulphur although they are unlikely to be commercially attractive for many years while abundant and cheap supplies of crude sulphur are available.

Anhydrite

In the United Kingdom, anhydrite deposits occur chiefly in the uppermost Permian rocks in the Tees-side area of south-eastern Durham and north-eastern Yorkshire, in Cumberland and in southern Yorkshire. Anhydrite is also found associated with some of the Triassic gypsum deposits occurring extensively throughout the East Midlands and with deposits of Upper Jurassic age in the south of England; it has also been recorded from relatively deep boreholes drilled in the Carboniferous Limestone in west Cumberland, Derbyshire and Leicestershire. On Tees-side very large reserves of anhydrite are present; in the Billingham area alone, reserves were reported in 1949 to be 70 to 75 million tons (71 to 76 million tonnes), assuming an average thickness of 4.5m and 56 per cent recovery. Substantial reserves are also present around Hartlepool and in Cumberland, while within an area of about 155 sq km around Goole in southern Yorkshire it is estimated that there may be some 1,500 million tonnes of anhydrite, again assuming a workable thickness of 4.5m.

Gypsum and phosphogypsum

Gypsum has the same general distribution as anhydrite in the United Kingdom and there are very large reserves, but its use for the manufacture of sulphuric acid is unlikely while large supplies of anhydrite are available. As in other industrial countries, gypsum is produced in the United Kingdom primarily for use in the preparation of plasters and Portland cement.

About 2 million tonnes of phosphogypsum derived from phosphoric acid manufacture was produced in the United Kingdom in 1971, nearly all of it being discharged as waste into the sea or into tidal estuaries, as is the practice at most European phosphoric acid plants. In the United Kingdom the impure nature of phosphogypsum produced has so far prevented its use in the manufacture of either sulphuric acid and its co-product cement or ammonium sulphate.

Pyrites

Pyrites is widely distributed in the United Kingdom, but none of the known occurrences is economically workable, the grade of the deposits formerly mined being generally low and variable. It occurs in notable quantities in the mineralised veins of south-western England and the Northern Pennine Orefield and as disseminations in coal. Pyrites is common also in the Lower Palaeozoic shales and slates of North Wales and in the graphitic slates of Pre-Cambrian (Dalradian) age in parts of the Scottish Highlands. Large quantities may be present in the waste produced by slate quarrying in Argyllshire.

Exploratory work on the Great Sulphur 'Vein' south of Alston, in Cumberland, carried out during the Second World War indicated that large tonnages of low-grade sulphide ore are probably present. The lode consists of iron pyrites, pyrrhotite, marcasite and, in places, accessory chalcopyrite and galena. Quartz gangue makes up at least half the lode. Earlier attempts to produce pyrites were not profitable and only very small quantities of argentiferous lead ore were produced between 1851 and 1863. The sulphide zone in the main level, re-opened in 1941, is about 6m thick and averages 9.5 per cent sulphur, the best 1.5m containing 24.7 per cent sulphur.

Coarse pyrites is the principal mineral impurity in coal and can be readily removed by conventional coal cleaning methods. Although large quantities are theoretically available, much of it is in a finely divided state and can only be removed by grinding the coal to a very small size. The average sulphur content of British coals is about 1.5 per cent, but there are considerable variations: about one-half of the sulphur appears to be in organic combination in the coal substance itself.

Industrial waste (flue) gases

Flue gases are desulphurised in the United Kingdom to reduce air pollution and the processes available at present are costly. The burning of fuels results in the emission of a complex mixture of both gaseous and particulate pollutants. Sulphur dioxide is normally used as a measure of pollution, but emissions may also contain sulphur trioxide, oxides of nitrogen, carbon monoxide, alkali salts, soot, hydrocarbons and various trace elements. Normally the SO_2 concentration is 0.1 to 0.2 per cent. The total amount of SO_2 emitted from fuel combustion in 1970, for example, was estimated to be 5.95 million tonnes, containing some 2.98 million tonnes of sulphur, of which coal-burning power stations contributed the equivalent of 1.07 million tonnes and oil-burning power stations some 260,000 tonnes.

Practicable steps to reduce the emission of sulphur oxides to the atmosphere are very desirable, particularly because they constitute a source of air pollution at ground level, as they are irritant, corrosive gases that can cause damage to building materials, metals and fabrics and in sufficient concentration can adversely affect health and plant life. In general, the problem of sulphur dioxide emissions from industrial flue gases has been tackled in the United Kingdom by discharging these gases through suitably tall chimneys to limit ground level concentrations. This policy together with changes which have taken place in the pattern of fuel use, has so far resulted in a decrease in concentrations of sulphur dioxide, in spite of an increase in the total amount of sulphur dioxide emitted. Since the early 1960's sulphur dioxide concentrations in the air have been measured over the country as a whole by the Air Pollution Division of the Warren Spring Laboratory, Department of Trade and Industry. The Alkali and Clean Air Inspectorate[1] of the Department of the Environment is responsible for administering emission requirements at certain defined works, of which 1,875 were registered in England and Wales and 188 in Scotland at the end of 1971.

There seems little prospect at present of reducing economically the sulphur content of coal below the level for washed coals, although methods of sulphur reduction are being investigated by the National Coal Board. Further development of coal preparation techniques may make it possible to increase the amounts of sulphur that can be removed.

Natural gas

North Sea natural gas is virtually free of sulphur compounds, with the exception of the Hewett field off Norfolk, which contains an average of 0.05 per cent H_2S. The gas-bearing zone is of Lower Permian age. A gas field was discovered onshore near Lockton in Yorkshire in 1966 in Permian Middle Magnesian Limestone at a depth of about 1,800m. The gas contains about 0.05 per cent H_2S and very small quantities of sulphur are being produced (*see* page 28).

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[1] Standards for gaseous and particulate emissions from various industrial processes, including emissions from smelters and sulphuric acid plants, are set by the Chief Alkali Inspector in the exercise of his powers under the Alkali, etc. Works Regulations Act, 1906, which requires that the best practicable means should be used to prevent the emission of noxious and offensive gases to the air. Sulphur dioxide arising from the combustion of coal is excluded from control by the Alkali Act.

Desulphurisation of fuel oil

Desulphurisation of the lighter fuel fractions is standard practice at many oil refineries in order to make the products marketable, but the desulphurisation of residual oils is much more difficult, requiring the installation of additional and expensive processing facilities.

Recovery of sulphur from residual fuel oils is not practised in the United Kingdom, since the importation of low-sulphur crude oil from such sources as North Africa and Nigeria renders the use of such facilities unnecessary at present. Low-sulphur crude oil will become available also from the North Sea. Residual fuel oils currently being produced in the United Kingdom contain up to 3.5 per cent sulphur, averaging about 2.6 per cent. In 1972 about 45 million tonnes was used as fuel for inland consumption, containing about 1 million tonnes of sulphur.

Depending on the sources of the crude oil as well as the way in which the sulphur is combined, the cost of desulphurisation may vary between 50p and 150p per tonne of fuel oil for each 1 per cent reduction in the sulphur content to about 1 per cent, below which costs rise sharply. Assuming an average sulphur content of fuel oil of 3 per cent, the cost of the easy part of desulphurisation (down to about 1 per cent sulphur) would probably be between 100p and 300p per tonne. On the basis of information received from the petroleum industry, the Chief Alkali Inspector in his 1968 (105th) Annual Report has estimated that the cost of reducing the sulphur content of residual fuel oils burned in the United Kingdom to below 1 per cent would be about £45 million a year, thereby preventing the escape to the air of about 1.2 million tonnes of SO_2 per annum. There is necessarily a high margin of uncertainty in this figure. Experimental limitations have been imposed by the City of London (Various Powers) (No 2) Act 1971 to restrict the amount of sulphur permissible in fuel oil to 1 per cent for new installations in London. Existing installations will have to comply by 1987.

Oil shale

Deposits of oil shale containing between 5 and 8 per cent sulphur occur in the Upper Jurassic Kimmeridge Clay which extends north-eastwards from Dorset to Norfolk and into Lincolnshire and Yorkshire. Total reserves are large and oil production and sulphur recovery were fully investigated by the petroleum industry more than 20 years ago. It was concluded that the sulphur could not be recovered economically from the highly sulphurous oils produced by distillation.

Blast furnace slag

Sulphur is present as calcium sulphide in blast furnace slag, generally containing less than 2 per cent sulphur, but no economically acceptable process for its recovery is known. Sales of slag in the United Kingdom exceeded 9 million tonnes in 1971, perhaps containing about 180,000 tonnes of sulphur. Granulated blast furnace slag is used in the manufacture of slag cements; it is also used as an aggregate in concrete.

Crude sulphur

Desposits of crude sulphur are not known in the United Kingdom, although the possibility of their existence cannot entirely be excluded. Sulphur replacing anhydrite has been recorded from core samples of anhydrite-dolomite rock from the Eskdale No 2 borehole in Yorkshire where it is associated particularly with fine-grained anhydrite which contains a considerable amount of carbonaceous matter. On the United Kingdom continental shelf, exploration for oil and gas has shown that Zechstein (Upper Permian) salt including domes and diapiric features is developed throughout most of the southern North Sea. Anhydrite is known to be present but crude sulphur has not yet been reported.

World resources

World resources of sulphur are extremely large and are adequate to meet probable demand for many years. Total reserves of sulphur in natural gas, sedimentary and salt dome deposits, petroleum, pyrites and sulphide ores are estimated by the US Bureau of Mines to amount to some 2,500 million tonnes. Another estimate indicates that the amount of sulphur potentially available may exceed 20,000 million tonnes if sources such as coal, anhydrite and gypsum and sea water are also taken into account.

The major sources of supply at present are crude sulphur from Frasch mines and sedimentary deposits, sulphur recovered from natural gas, and pyrites. Frasch sulphur produced from the Mexican Gulf is likely to remain an important source of supply for some time, although it no longer dominates the world market as it did in the past, chiefly because of the rapid development of the natural gas industry in Canada, as well as the appearance of other sources of sulphur supply, such as Poland, France and, more recently, Iraq. Salt domes have been estimated to contain some 250 million tonnes of sulphur, but it appears unlikely that any further large commercial sulphur deposits will be discovered in the Mexican Gulf area since intensive exploration carried out over the last 10 years by the major Frasch sulphur producing companies has had relatively little success. In addition, any deposits found in the Gulf Coast offshore area may prove to be too costly to mine, as operating costs are at least 1½ to 2½ times as high as those of comparable onshore mines. However, other sources of primary crude sulphur have been developed or are planned to come into production. In western Texas, for example, reserves have been placed at about 100 million tonnes, while deposits in Poland are estimated to contain at least 90 million tonnes. Deposits associated with the Mishraq dome near Mosul,Iraq,estimated to amount to more than 200 million tonnes came into production at the beginning of 1972.

Elemental sulphur recovery from natural gas and oil refinery gases has increased markedly in recent years and has been chiefly responsible for creating the surplus of sulphur on the world market since 1968. Reserves of natural gas are large; according to the Canadian Petroleum Association proved reserves of sulphur in Canada at the end of 1971 amounted to some 150.2 million tonnes, nearly all of which was contained in Alberta. Sour natural gas is also being increasingly utilised in the Middle East. In Iran, for example, the recovery unit installed at Bandar Shahpur on the Persian Gulf is one of the largest in the world with a capacity of about 500,000 tonnes of sulphur a year. At Kirkuk in Iraq, a recovery plant capable of producing about 120,000 tonnes of sulphur a year from natural gas resumed operations in 1971. Plans have been reported for the production of sulphur from natural gas in the USSR, while in northern Germany the exploitation of sour natural gas fields is expected to raise total domestic production of sulphur to about 600,000 tonnes a year by 1975. Fuel oil is a large potential source of sulphur, but desulphurisation on a commercial scale only began in 1967, when the Chiba plant in Japan came into operation.

Heavy oil-sands, commonly known as 'tar' sands, constitute a very large potential source of sulphur. They occur extensively in northern Alberta, for example, where the Athabasca deposits have been estimated to contain some 780 million tonnes of sulphur. The deposits have an average sulphur content of nearly 5 per cent.

Uses

Sulphur is a vital industrial raw material, entering into many processing and manufacturing industries (Fig 1), its most important use in the United Kingdom and indeed in all industrialised countries being in the manufacture of sulphuric acid (*see* below). Sulphur is also used extensively in the rayon, pulp, paper, dyestuffs, pharmaceutical and rubber industries. Initially it was used in religious ceremonies, for fumigating buildings and for bleaching cloth. Sulphur appears to have been used in Egypt in 2000 BC to bleach linen textiles and may have been used by the Egyptians even earlier to produce sulphuric acid which was used to make nitric acid for dissolving silver. The Romans found uses for it in medicine and warfare. It is an essential constituent of gunpowder.

Sulphur has an important use in 'vulcanising' rubber based on Goodyear's discovery in 1839 that by heating rubber with sulphur, the rubber lost its natural stickiness and could be found many new applications. From about 4 to 30 per cent sulphur is generally present, the higher proportions being used when harder varieties of rubber are required. Finely ground crude sulphur is used for this purpose, and is important also in agriculture as a fungicide, chiefly to protect vines, fruit, trees and vegetables from mildew, and is used in organic insecticides and acaracides. Sulphur is indispensable as a plant nutrient, sulphur and its compounds being applied directly to the soil and as constituents of some fertilisers. Sulphur deficiency causes a yellowing of foliage, so that plant growth is retarded and there is a slowing down in the ripening of fruit. The element plays a part in the synthesis of plant protein and also appears to act as a catalyst in the synthesis of chlorophyll. Sulphur is used in making carbon disulphide, which is extensively used in rayon manufacture, and in the preparation of acid-resisting cements. Sulphur ointments have been used in treating skin infections. As liquid sulphur dioxide, it is used as a refrigerating agent and foodstuffs preservative, in the preparation of dyes, as a disinfectant and for bleaching silk and wool. Sulphur dioxide is also much used for manufacturing calcium disulphide, used in the preparation of wood-pulp for paper manufacture. As a constituent of antimony sulphide, sulphur is used in the manufacture of safety matches.

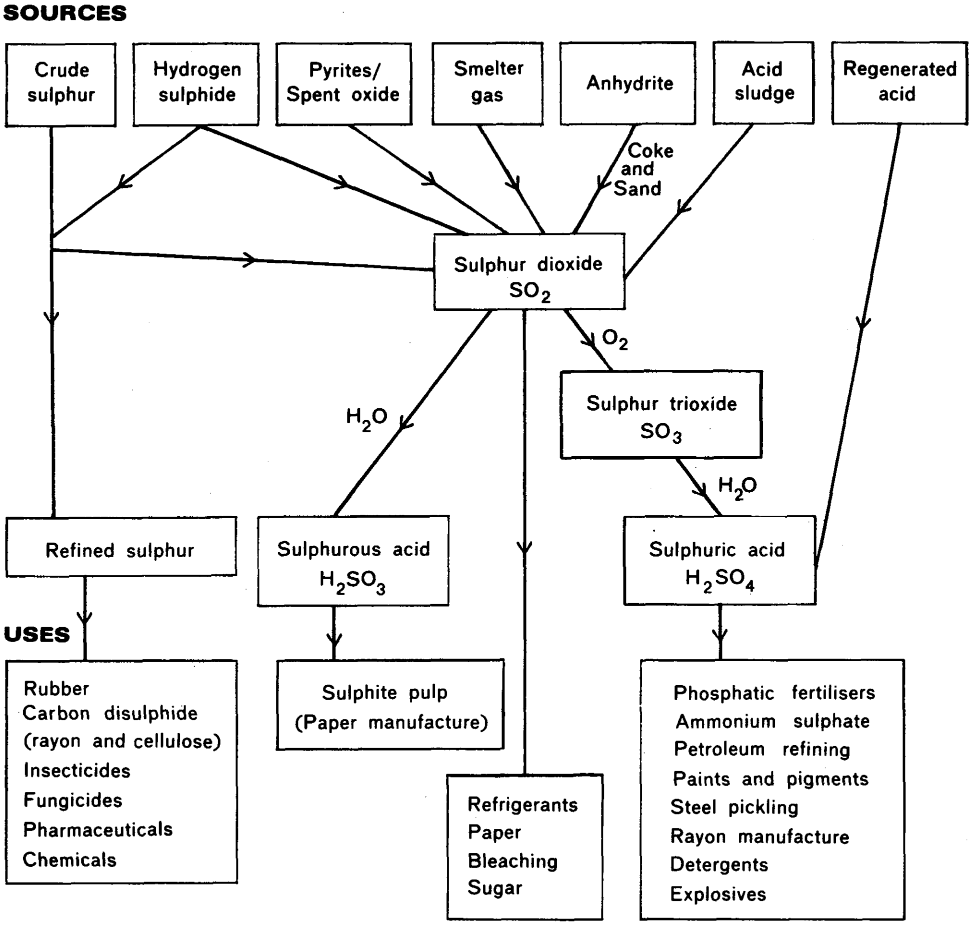

Fig 1 Sources and uses of sulphur

New applications have been developed or are being investigated, particularly in Canada and the USA, which may provide important new commercial outlets. For example, a mixture known as 'Thermopave' containing 13.5 per cent sulphur, 6.0 per cent asphalt and 80.5 per cent sand has been developed by Shell Canada Limited and tested as a base course in road construction. The sulphur is said to impart strength and give a fast set, as well as resistance to deformation, and to allow the use of sand instead of crushed rock in the mix. It has been suggested that in Canada there might be a potential requirement of more than 600,000 tonnes of sulphur per annum for use in such mixtures. It has also been suggested that rigid sulphur foams could compete favourably with plastic foams for some uses, including the insulation of the subsoil under roads to minimise frost-heaving problems in very cold climatic conditions and, under similar conditions, to facilitate the construction of, say, pipelines and aeroplane runways.

A number of sulphur-bearing constructional materials, including sulphur concretes, have been proposed and tested, as have sulphur-based traffic paints, in both instances making use of sulphur's resistance to water, acids and solvents. Research has been conducted on impregnating porous materials, such as concrete, ceramics, wood and paper, and into the use of sulphur in the preparation of plastics and polymers. It is reported that a small market has been developed in Europe and Japan for sulphur used to impregnate ceramic tiles.

Sulphuric acid

Sulphuric acid is one of the most widely used of commercial chemical materials and is used at some stage in the manufacture of most industrial products. Its importance led the great German chemist Justus von Liebig in the mid-19th century to conclude that the commercial prosperity of a nation could be measured by the amount of sulphuric acid it consumed. Sulphuric acid has great affinity for water, making it a powerful dehydrating agent, and it is also a valuable electrolyte, a strong oxidising agent and a solvent in which many important chemical reactions can take place. It is used in different concentrations varying from extremely dilute solutions to the highly concentrated fuming acids (oleum) which are produced for the manufacture of drugs, dyes and explosives. Most commercial sulphuric acid produced in the United Kingdom contains 96 to 98 per cent H_2SO_4.

The preparation of sulphuric acid either from calcined copperas (ferrous sulphate) and silica or by burning a mixture of sulphur and saltpetre was apparently first described in the United Kingdom during the 15th century. Before the 18th century sulphuric acid was used mainly in alchemy, although Glauber's 'sal mirabile' was prepared for medical purposes by adding sulphuric acid to common salt.

Sulphuric acid has been produced in the United Kingdom on an industrial scale since 1746, when John Roebuck and his partner Samuel Garbett established a factory in Birmingham. Production was based on burning a mixture of crude Sicilian sulphur and saltpetre (potassium nitrate). The acid was used in tin-plate making, brass founding, button manufacture and in refining precious metals, its function being primarily to clean metals or to remove copper from silver. Sulphuric acid was used also to make dyes for textiles and in the manufacture of chlorine after about 1799 when chlorine bleaches were introduced. For many years sulphuric acid formed the basis of the Leblanc soda process which was established in the United Kingdom in 1823 and led to the development of the important British alkali industry.

The largest single use of sulphuric acid in the United Kingdom today is in the manufacture of phosphatic fertilisers, some 1.2 million tonnes being consumed for this purpose in 1972. Industries which each used more than 100,000 tonnes of acid accounted for about 96 per cent of the total of 3.8 million tonnes consumed, as shown in Table 1. The consumption of sulphuric acid by major uses for the period 1962-1972 is shown in Fig 2. Of the other uses, the most important was the production of hydrofluoric acid.

About 80 per cent of the sulphuric acid produced is used captively, major users such as fertiliser and chemical manufacturers usually operating their own acid plants at sites determined by proximity to major markets or to other raw materials, as the transportation of sulphuric acid is expensive in relation to its low cost of manufacture. Distribution is generally by road and rail tanker and in some circumstances large bulk shipments of sulphuric acid by sea have become an integral part of the market. International trade amounted to nearly 2 million tonnes in 1972.

Table 1 United Kingdom: Consumption of sulphuric acid, 1972

Trade Uses	*Tonnes 100 per cent H_2SO_4*	*Percentage of total*
Fertilisers and agriculture, including 987,057 tonnes for phosphatic fertilisers 216,436 tonnes for sulphate of ammonia	1,215,790	31.8
Paint and pigments	605,151	15.8
Natural and man-made fibres and transparent cellulose film	496,784	13.0
Chemicals including 144,243 tonnes for plastics 94,163 tonnes for sulphates of alumina, barium, copper, magnesium and zinc 80,884 tonnes for hydrofluoric acid 41,124 tonnes for hydrochloric acid	483,405	12.7
Detergents and soap	382,100	10.0
Metallurgy including 112,748 tonnes for steel pickling	120,721	3.2
Dyestuffs and intermediates	93,774	2.5
Oil and petrol	47,679	1.2
Miscellaneous	374,207 *(a)*	9.8
Total	3,819,611 *(b)*	100.0

(a) Includes 12,225 tonnes for exports

(b) Total includes 149,984 tonnes of imported acid and 180,378 tonnes of recovered acid

Source: The National Sulphuric Acid Association Limited.

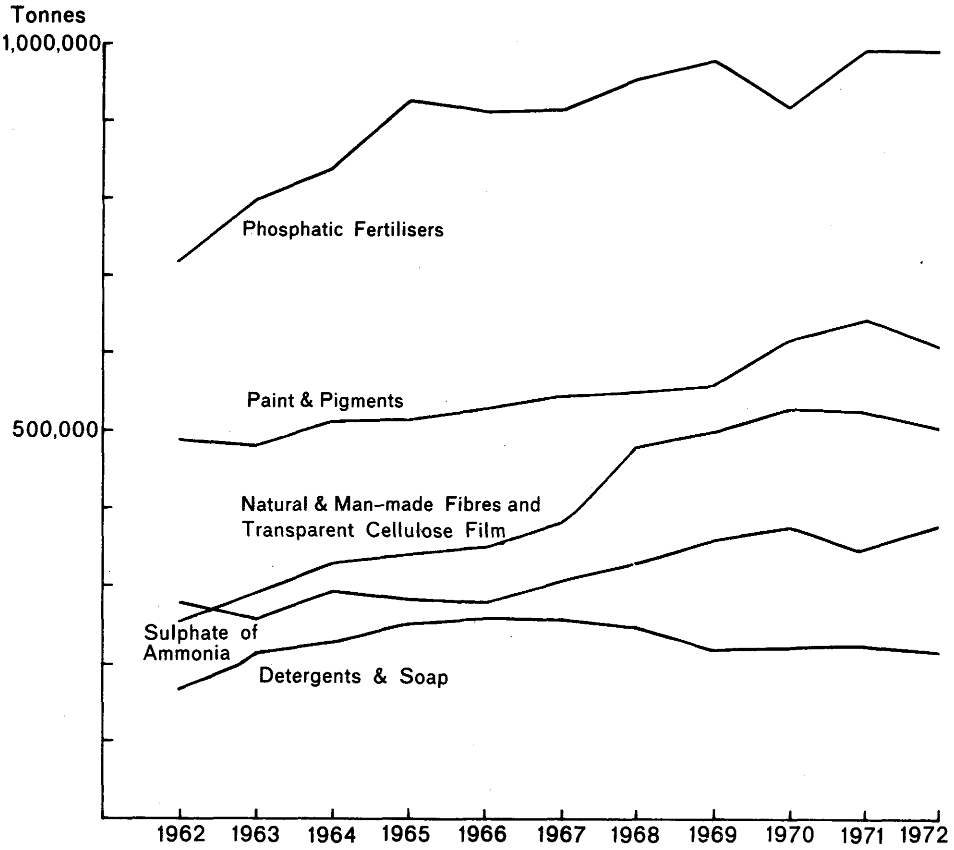

Fig 2 United Kingdom consumption of sulphuric acid, by major industries, 1962-1972

Specifications and marketing

Commercial sulphur is a comparatively pure product, invariably containing more than 99 per cent sulphur (dry basis). It is sold in dry bulk form or as liquid or in an increasing variety of formed products such as granules, pellets, flakes and slates. However, the trade recognises several impurities or contaminants of which the most important are ash, hydrocarbons, sulphuric or sulphurous acids, arsenic, selenium, tellurium and moisture.

Two grades of Frasch sulphur are marketed: ***bright sulphur,*** a bright yellow crude sulphur, which should not contain more than 0.08 per cent carbon, and brownish ***dark sulphur*** which should not contain more than 0.25 per cent carbon. Bulk sulphur shipments generally contain less than 0.010 per cent ash and even smaller percentages are present in sulphur produced from sour natural gas or refinery gases. Frasch sulphur invariably contains much less than the maximum of 0.25 ppm by weight of arsenic and less than the maximum of 2.0 ppm for both selenium and tellurium, the tests and specifications for which originated when the principle source of sulphur for sulphuric acid manufacture was pyrites and other metalliferous ores. Elemental sulphur recovered from natural gas is marketed in the form of bright sulphur. Pyrites as sold normally contains at least 48 per cent equivalent sulphur.

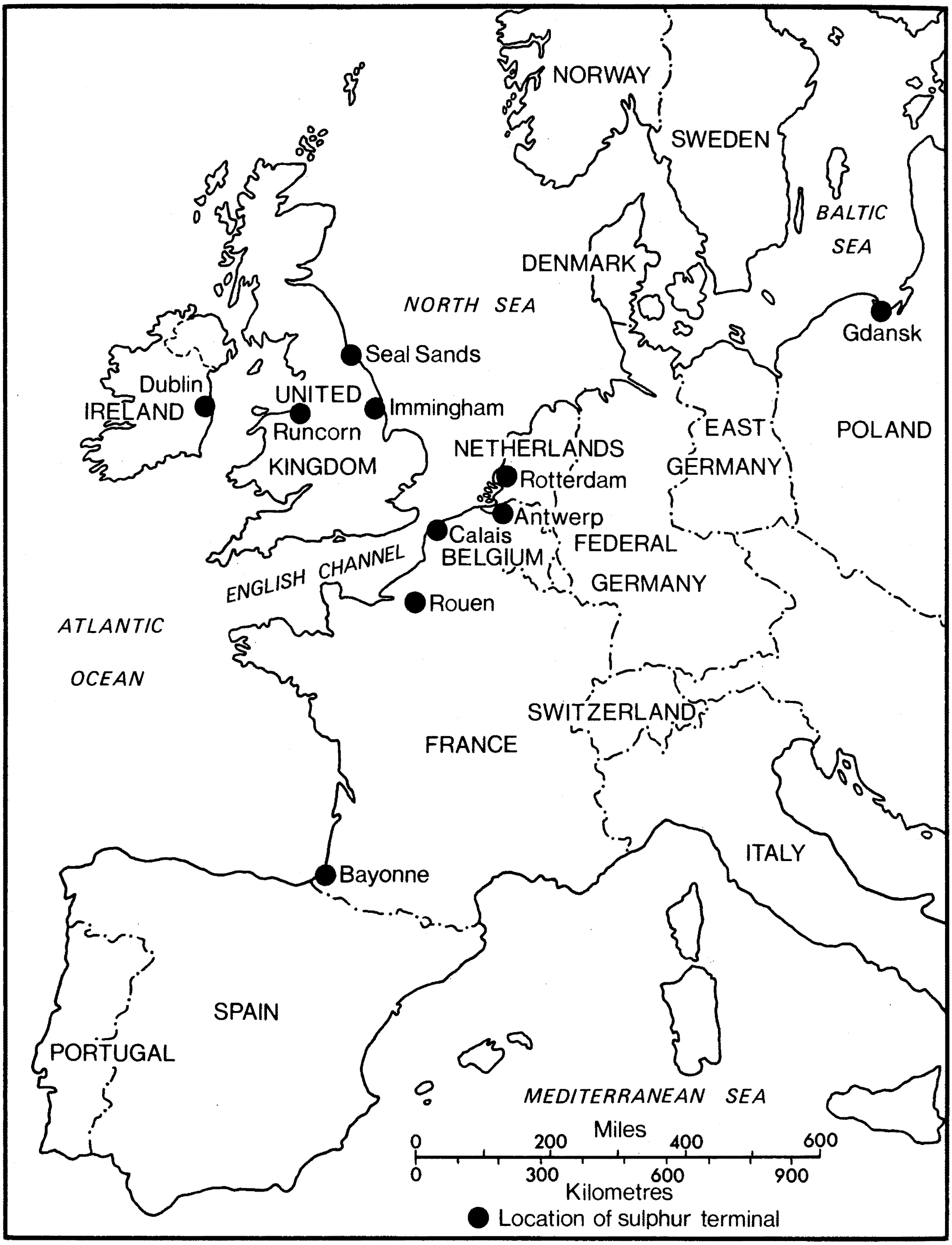

Fig 3 Location of solid and liquid sulphur terminals in Europe

A recent development is the marketing of sulphur in the form of 'slates'. The first slating plant was built for Shell Canada Limited at its gas processing plant at Waterton, Alberta, and has been in operation since August, 1970. Molten sulphur is poured on to a liquid-cooled conveyor belt on which the sulphur solidifies and breaks up into 'slates' or platelets some ¼ in (6 mm) thick and roughly 6 in (15 cm) across as it leaves the conveyor belt. This process, which was developed and patented, in 1970, by the Canadian firm Vennard and Ellithorpe Limited is the most successful of the various methods tested by producers in Canada, as it largely eliminates the problem of dust which arose during loading and the consequent need to use water-sprays. Slate-forming facilities have since been installed at many major Canadian sulphur plants. Another innovation is the development in the United Kingdom of the 'Sulpel' process by Elliott Associated Developments Limited. The process produces hard, spherical sulphur pellets, which are claimed to be waterproof, dust free and unaffected by climatic conditions. Pelletising facilities using the process have been installed at oil refineries in Curaçao, Singapore and the Virgin Islands.

In Europe there are 15 terminals at 10 ports for storing and handling solid and liquid sulphur which are operated by the major North American, French and Polish suppliers (Fig 3). Nearly all Frasch sulphur is shipped in liquid form, or is melted on arrival in Europe pending delivery to customers. Exports of liquid sulphur from the USA began in 1964 and about 95 per cent of US sulphur is now transported in this form.

Price

Sulphur is usually sold under long-term contracts, prices having been dominated by the Mexican Gulf Frasch sulphur producers until 1968, when Canada became the principal exporter of crude sulphur and there was also an expansion of very competitively priced Polish sulphur shipments to western Europe. Most export sales from the USA are organised by the Sulphur Export Corporation (Sulexco), New York. Price ranges for Frasch sulphur delivered in the United Kingdom at the end of 1972 are shown below, those relating to shipments of liquid sulphur to customers in north-west Europe being based on Sulexco's declared price for bright sulphur at $27 per long ton (£11.31 per tonne), ex-terminal Rotterdam. Competitive prices were established by other suppliers of liquid sulphur to north-west Europe, including Duval Sales International SA, the Canadian Sulphur Export Limited (Cansulex), Société Nationale des Pétroles d'Aquitaine (SNPA), the Polish organisation Ciech-Siarkopol, and the Mexican Azufrera Panamericana SA. Export prices of dry, bulk sulphur from the US Gulf area were based on $20.50 per long ton (£8.58 per tonne) fob for bright sulphur, which commands a premium of $1.00 per long ton (42p per tonne). Dry bulk sulphur prices in western Europe were on the basis of $20 per long ton (£8.38 per tonne), c and f, depending on vessel size and port of delivery.

Delivered price ranges for US Frasch sulphur, late 1972

Marketing area	*$ per tonne c and f*	*Equivalent sterling per tonne (a)*
North-west Europe (liquid)	23 – 27	9.79 – 11.49
North-west Europe (solid)	20 – 23	8.51 – 9.79
Mediterranean	25 – 26	10.64 – 11.06
Latin America	25 – 29	10.64 – 12.34
South-east Asia/Far East	22 – 27	9.36 – 11.49

(a) Converted at $2.3502 to £1 sterling

Source: The British Sulphur Corporation Limited.

Cansulex, which was established in 1962, markets the output of some 22 producers in Canada, although bright sulphur produced by Shell Canada Limited, one of the largest producers of sulphur in western Canada, is sold separately by International Sulphur Company Limited, Alberta. Deliveries of Canadian sulphur overseas are made in the form of slates only and were priced on the basis of $14.50 – $15.50 per long ton (£6.07 – £6.49 per tonne) fob Vancouver. Supplies from Poland, Mexico and France are priced competitively. US domestic list prices for Frasch sulphur, most of which is shipped in liquid form, are generally quoted per long ton, dark sulphur, bulk, fob,cars, mines, fob, vessels, Gulf port; and fob,regional terminal.

The authorised export price of European pyrites, although related to Frasch prices, is based essentially on that of Rio Tinto (Spanish) crude fines, fob, Huelva, 48 per cent S (dry weight) taking into account variations in grade and the value of metallic residues. Sales in 1972 were at £3.60 per tonne fob, Huelva, less a contribution of £0.30 in respect of residues.

Since the Second World War the world sulphur industry has experienced two periods of short supply and one of over-supply. An acute sulphur shortage around 1950, induced by the Korean war, led to an increase in world production capacity which, in turn, gave rise to a worldwide surplus. Sulphur prices reached very low levels in 1963 and 1964, when there was a stockpile of Frasch sulphur equivalent to about 43 weeks' supply. Although new Frasch deposits in Mexico had been brought into operation and plants were constructed in France and Canada for the recovery of sulphur from sour gas, there was a sulphur deficit during the period 1964-1968 and stockpiles of Frasch sulphur were reduced to only 12 weeks' supply. Prices rose steeply from 1964, reaching record levels by 1968; quotations for Canadian sulphur in early 1968 ranged from $45 to $55 per long ton fob Vancouver. However, the slowing down in the growth of demand of sulphur by the phosphatic fertiliser industry and the entry of Polish and Canadian sulphur on the world market on a large scale, resulted in another surplus in the Western World of about 500,000 tonnes in 1968, and after the second half of 1968 prices fell markedly because of the abundant supplies of sulphur which have become available, particularly from 'sour' natural gas and oil refineries. The supply-demand situation again changed significantly during the second half of 1972, following the decision by the Vancouver port authorities to prohibit the handling and loading of dry bulk sulphur after the 1st July,1972.because of the problems associated with sulphur dust,until adequate facilities for shipping and storing sulphur slates were installed. Hitherto a large proportion of Canadian exports had been in the form of dry bulk sulphur recovered from vats.

Factors which have an important bearing on the future price of sulphur are the extent to which the so-called 'involuntary' sulphur becomes available on the world market and the progress made with clean air legislation. 'Involuntary' sulphur is made available by producers who are obliged to remove sulphur from natural gas or oil in order to make their products marketable. Production of this sulphur is, therefore, determined by the demand for natural gas and oil, regardless of the world sulphur market, and in consequence has created a competitive environment in an industry previously dominated by the Mexican Gulf Frasch producers.

Technology

Commercially the most important processes in the sulphur industry are those which produce high-grade elemental sulphur or crude sulphur from salt dome deposits (Frasch process) and those involving the recovery of either H_2S from natural gas or SO_2 made available at metal smelters. In some countries use is also made of the sulphur values contained in anhydrite or gypsum and phosphogypsum. Most of the sulphur or sulphur compounds obtained are used to produce sulphuric acid. Much research has been and is being devoted to the recovery of sulphur from industrial waste gases but no economic process has yet been developed.

Frasch sulphur

The well established hot-water process used for mining sulphur deposits associated with salt domes was developed by Herman Frasch of the Standard Oil Company. Patents on the process were applied for in 1890 and the first Frasch sulphur mine came into operation in Louisiana in 1894. The Frasch process is based on the fact that crystalline sulphur melts at about 116°C. Wells drilled into the sulphur-bearing beds are equipped with four concentric pipes typically 8 to 10 in, 6 in, 3 in and 1 in (20.3 to 25.4, 15.2, 7.6 and 2.5 cm) in diameter. In 'steaming' a well, superheated water at about 175°C is pumped down the annular space between the 6-in and 3-in pipes and is discharged into the sulphur-bearing formation through perforations in the 6-in pipe. The zone through which the water circulates is raised to a temperature above the melting point of sulphur. Compressed air is injected through the central 1-in pipe into the molten sulphur and raises it to the surface in the outer annulus. Liquid sulphur reaching the surface is discharged into steam-heated tanks from which it is pumped into vats, where it is stored in either dry or liquid form. As each well is only effective over a limited area new wells are constantly being drilled. In addition, bleeder wells have to be drilled to remove the excess cool water that accumulates within the sulphur-bearing formation or to reduce excessive pressures. Generally, wells have a life ranging from a few days to two years, averaging about one year, and about 35,000 tonnes of sulphur can be extracted before the cavity becomes too large for effective production. The most important cost factor is the 'water ratio', which is the quantity of hot water required to recover one tonne of sulphur and determines the maximum production rate that can be sustained from a given boiler plant. Water ratios range from about 3,700 litres to as much as 45,400 litres per tonne of sulphur recovered.

Similar techniques are used to extract sulphur from stratified deposits not associated with salt domes, such as those worked in south-eastern Poland. In Poland, however, part of the output is derived also from opencast workings using draglines and bucket-wheel excavators, the sulphur ore being transported by conveyor belt to a crushing plant and then upgraded by flotation. The concentrate, which contains about 84 per cent sulphur, is melted at 150°C and filtered to yield a marketable product containing 99.5 per cent sulphur. About 0.4 tonnes of filter cake with some 40 per cent sulphur is obtained per tonne of crude sulphur processed and is used in the manufacture of sulphuric acid. Comparable methods of beneficiating low grade sulphur ores are in use in a number of other countries.

Natural gas and crude oil refining

Absorption processes based on its acidic nature are employed in recovering hydrogen sulphide (H_2S) from sour natural gas or oil refinery gases. Amines, chiefly diethanolamine, are the most widely used absorbents; others include potassium carbonate, sodium phenolate, sodium carbonate and sodium thioarsenate. Normally, between 90 and 95 per cent of the hydrogen sulphide is removed. In one of the best known methods, the Girbotol process, regenerated absorbent solution flows through scrubbing towers against the gas stream. The H_2S is released by steam stripping or reboiling in another tower and may be used for the production of elemental sulphur or oxidised to sulphur dioxide for sulphuric acid manufacture. For conversion to elemental sulphur a method based on the Claus-Chance process is generally employed, involving the burning of about one-third of the hydrogen sulphide gas in a catalytic reactor where the hydrogen sulphide and sulphur dioxide react to form elemental sulphur and water vapour. Up to 90 per cent of the sulphur may be recovered with this process.

The increasing demands for low-sulphur fuels have prompted much research and development work on the desulphurisation of various petroleum fractions. The most advanced method adopted for reducing the sulphur content of fuel oils is known as hydrodesulphurisation, the principle involved being simply to convert all the bound sulphur to hydrogen sulphide. This is accomplished by treating the heated fuel oil with hydrogen in the presence of a suitable catalyst, generally at a temperature of between 345 and 455°C and at a pressure of 500 to 3,000 psi (35 to 211 kg/cm^2). Processes developed in recent years which have been adopted commercially are capable of treating entire oil residues to produce low sulphur products; in one technique the sulphur content of heavy fuel oil is reduced from about 3.9 to 1.0 per cent and recovered.

In 'tar' sands such as the Athabasca deposits found in north-eastern Alberta, most of the sulphur is present as complex compounds which can be desulphurised to produce H_2S. The hydrogen sulphide is then converted to sulphur in the same way as that recovered from natural gas.

Sulphide concentrates

Sulphur dioxide (SO_2) is produced when metallic sulphide concentrates are roasted to produce the metallic oxide. Pyrites may be roasted in multiple hearth, fluidised bed or flash-type calciners, conditions depending on whether the desired product is the calcine and its contained metallic values or sulphur dioxide, or both. In one well-established process pyrites concentrates are roasted with air in vertical furnaces composed of several stacked hearths fitted with mechanical rakes, from which they emerge as a calcine, cinder or spent oxide. The average roasting temperature is around 900°C. Secondary reactions may occur if other metallic sulphides, such as those of copper or zinc, are present and these may also exert some influence on the roasting temperature selected. Recovery of the maximum theoretical sulphur dioxide content of 14 to 16 per cent is possible from either iron or zinc sulphides. The recovery of waste heat from roaster exhaust gases is also important; from 1 to 1½ tonnes of steam can be recovered per tonne of pyrites containing 50 per cent sulphur. After cleaning, cooling and drying, the SO_2 is used in the manufacture of sulphuric acid.

The fluidised-bed process, which was developed simultaneously in the USA and Germany during the Second World War, is much more effective than the earlier processes for roasting pyrites. It involves the suspension of solid particles in an upward-rising stream of gas, resulting in a violently agitated or fluidised mass. It permits close control of the roasting temperature, prevents overheating or fusion of metallic sulphides and enables a concentrate with only 25 per cent sulphur equivalent to be used, as opposed to a minimum of 35 per cent with the multiple-hearth roaster. Copper and zinc sulphides can also be roasted to produce gas containing 10 to 14 per cent SO_2. Flash-roasting is a similar process particularly applicable to fine solids which involves the combustion of sulphide flotation concentrates while suspended in air. Pyrites concentrates produced as tailings in the flotation of a mixed sulphide ore may be flash-roasted in a specially designed furnace to yield elemental sulphur and pyrrhotite, which is then roasted to produce sulphur dioxide, the calcine being made into pellets for use as blast furnace feed. The Orkla process was developed in Norway to produce elemental sulphur and a copper matte from cupriferous pyrites, using a water-jacketed blast furnace.

Concentrates of zinc sulphide (zinc blende or sphalerite) are commonly roasted in the same way as pyrites, yielding gas with a relatively uniform SO_2 content. Production of sulphuric acid from SO_2 with gases obtained in processing lead concentrates (chiefly of galena, PbS), which usually contain only about 15 per cent sulphur, is normally only practicable if the installation is large or if it is associated with zinc smelting. At Avonmouth, for example, mixed concentrates with 36.6 per cent zinc, 18.3 per cent lead, 23.0 per cent sulphur and 1.5 per cent copper have been used in the Imperial Smelting process. Gases containing about 6 per cent SO_2 are scrubbed and cleaned before being passed through a series of heatexchangers into the converter, where sulphur dioxide is oxidised to SO_3 in the presence of a catalyst. The SO_3 is dissolved in absorbers to form sulphuric acid.

Copper concentrates (as chalcocite, Cu_2S and chalcopyrite, $CuFeS_2$) may contain up to 40 per cent sulphur but the SO_2 content of the smelter gases varies considerably and recovery is generally more complicated. Recovery of sulphur is being carried out at an increasing number of copper smelters, however, to comply with the increasingly stringent air pollution regulations now being introduced.

Anhydrite and gypsum

There are four main inorganic processes for recoverying sulphur from anhydrite or gypsum. Anhydrite is used where possible since with gypsum more fuel is needed to eliminate the water it contains. The two processes which have been in commercial use for many years produce either sulphuric acid and cement clinker by calcination (the Müller-Kühne process) or ammonium sulphate by double decomposition. They are based essentially on pioneer development work carried out in Germany during the First World War at Leverkusen which was subsequently continued in the United Kingdom by Imperial Chemical Industries Limited.

The Müller-Kühne process, which is employed in the United Kingdom and Austria, consists of roasting ground anhydrite, clay, sand and coke to a temperature of between 1200 and 1400°C in rotary kilns, the calcium sulphate being reduced to lime which combines with the rest of the charge to form cement clinker. Gases containing up to about 9 per cent SO_2 are produced which are passed through a cyclone to collect dust and then through an elaborate purification system before being converted to sulphuric acid. The reaction can be expressed empirically as follows:

$$2CaSO_4 + C \rightarrow 2CaO + 2SO_2 + CO_2$$

About 0.95 tonne of cement clinker is produced with every tonne of acid from 1.7 tonnes of anhydrite.

The double decomposition process is based on the following reaction between calcium sulphate and ammonium carbonate:

$$CaSO_4 + (NH_4)_2CO_3 \rightarrow CaCO_3 + (NH_4)_2SO_4$$

Ammonia and carbon dioxide are passed into a slurry of finely ground anhydrite or gypsum to form ammonium carbonate, which reacts with calcium sulphate to give calcium carbonate and ammonium sulphate, the latter dissolving in water. At the end of the reaction the 25 per cent ammonium sulphate solution is filtered off from the insoluble calcium carbonate and concentrated in evaporators to crystallise out the ammonium sulphate. Plants using this process have been operated on a large scale in the United Kingdom (until April, 1971) and Austria and, using gypsum, in Italy, Turkey, India and Pakistan. Ammonium sulphate is used chiefly as a fertiliser, while the calcium carbonate may be used in the manufacture of cement and the fertiliser calcium ammonium nitrate (a granular mixture of ammonium nitrate and calcium carbonate). The commercial feasibility of this process depends to a large extent on the economic use of the waste calcium carbonate.

In a third process, calcium sulphate (gypsum) is reduced to calcium sulphide from which H_2S is produced and converted to sulphur. An attempt was made to use this process at a plant completed in 1968 by the Elcor Chemical Corporation near Van Horn, western Texas, the availability of cheap fuel in the form of natural gas being an important factor. A fourth method is the reduction of calcium sulphate with carbon monoxide to produce sulphur dioxide (SO_2) and lime (CaO).

Spent oxide

Spent oxide is obtained when coal gas and coke-oven gas are purified with iron oxide in order to meet the statutory limit of 1.5 parts per million of hydrogen sulphide set for gas supplied for domestic use. The gas is passed through the iron oxide in purifier chambers where the H_2S is absorbed and the oxide converted to iron sulphide. By introducing regulated quantities of air into the gas the sulphide is continuously re-oxidised to iron oxide and elemental sulphur. Ultimately the sulphur content becomes so high that the iron oxide material is no longer effective and has to be removed. Usually such spent oxide received at sulphuric acid works contains about 45 per cent sulphur. One of the main advantages is that sulphuric acid free from arsenic can be produced from most spent oxides. Normally the spent oxide is roasted in much the same way as pyrites, producing gases containing 6 to 7 per cent SO_2; the elemental sulphur can also be extracted with a solvent, carbon disulphide. A number of other processes are technically feasible for desulphurising coke-oven gas and a few have been used on a commercial scale. These include liquid processes, such as ammonia washing, and the Stretford process which involves oxidising the H_2S to elemental sulphur in the presence of an organic catalyst, the sulphur being then removed by filtration or centrifuging.

Phosphogypsum

Phosphogypsum is produced as a waste product during the preparation of phosphoric acid by the 'wet' process, in which phosphate rock is digested with sulphuric acid. Approximately 5.5 tonnes of phosphogypsum is made available per tonne of P_2O_5 in the phosphoric acid produced, presenting a waste disposal problem. Phosphogypsum is used on a commercial scale in the production of sulphuric acid and cement clinker is South Africa at Phalaborwa, in northeastern Transvaal. Elsewhere there is growing interest in its use primarily as a means of solving the disposal problem. Its disadvantages compared with either anhydrite or natural gypsum are its high water content, fine particle size and frequently inconsistent quality. In addition, phosphogypsum may contain between 0.4 and 1.5 per cent P_2O_5 and up to about 1.5 per cent fluorine, both of which are objectionable for cement manufacture. Traces of radioactive material may also be present. Modifications to the process have been made, however, which apparently overcome these difficulties.

Industrial waste (flue) gases

Power plants burning coal or fuel oil emit large quantities of flue gas commonly containing appreciable quantities of sulphur dioxide (SO_2). Although the concentration is generally less than 0.1 per cent, there is interest in some countries in reducing it still further in order to minimise air pollution. Sulphur is not recovered at present, however.

Several processes have been developed for the removal of SO_2 from power station flue gases, and two of these have been operated on a commercial scale in the United Kingdom. The *Battersea process,* which has been used in London at Battersea since 1935, and subsequently at Bankside, is an effluent process requiring large quantities of water, to which chalk is added, about 30 to 35 tonnes of water being needed to wash each tonne of fuel burned. About 92 to 97 per cent of the sulphur dioxide is removed. The water is returned to the River Thames, together with calcium sulphate contained in solution. The use of the process at one of the Battersea stations was discontinued in 1969 for an experimental period, and the results of monitoring which was completed in May, 1972, are being assessed.

The Howden - ICI or *Fulham process* was first installed at Tir John, near Swansea, and later at the Fulham power station. It employed a recirculating suspension of lime and differs from the Battersea process in that it does not give rise to large quantities of liquid effluent, but yielded large quantities of sludge, containing 67 per cent calcium sulphate and 12 per cent calcium sulphite, which was dumped at sea. The process was abandoned in 1939 before a satisfactory method of overcoming scale formation by calcium sulphate had been devised.

Sulphur cannot be recovered economically in the processes in which sulphur dioxide is absorbed with lime, but other processes have been tested in the United Kingdom. In 1939 tests led to the development of the non-effluent Fulham-Simon-Carves process which employs an ammonia solution instead of lime to recover the sulphur directly in more useful forms, an essential step in the process being the conversion of ammonium sulphite to ammonium sulphate and sulphur in an autoclave. This work was delayed by the war but further research was undertaken after 1948 by the former Fuel Research Station in collaboration with Simon-Carves Limited and the then Central Electricity Authority. The process was based originally on ammonia liquid from gas works and a pilot plant was installed at the North Wilford power station, Nottingham. No method of overcoming corrosion in the autoclave was evolved before the process was abandoned because of the unfavourable costs.

None of these 'wet' processes has proved satisfactory, because they cool the flue gases and thus hinder their dispersion. Dry processes are therefore preferable and a number have been under development, notably in the United Kingdom, USA, Japan and the Federal Republic of Germany. In the United Kingdom a process developed by the US Bureau of Mines for absorbing sulphur dioxide on sodium aluminate granules has been investigated in detail by the Central Electricity Generating Board. It employs a three-stage fluidized-bed reactor for the removal of 95 per cent of the sulphur in flue gases entering at about 120°C. Spent absorbent is sent to a regenerating system which is fed with reformed low-pressure gas and produces H_2S for conversion to sulphuric acid in a Claus plant (*see* page 19). There are no plans for commercial development at present, however, because of the difficulty of manufacturing granules with consistent performance in the process. Processes developed in other countries based on adsorption of sulphur dioxide in active carbon, in potassium sulphite solution or suspensions of magnesia, and on the catalytic conversion to sulphur trioxide and recovery of sulphuric acid are commercially available, but they are expensive in both capital and operating costs, which are unlikely to be offset to any substantial extent by the market value of the sulphur or sulphuric acid recovered.

Sulphuric acid

The first stage in the manufacture of sulphuric acid is the production of sulphur dioxide (SO_2) gas, which is then oxidised to sulphur trioxide (SO_3) by two different techniques, the contact and lead chamber processes, each employing catalysts.

The *contact* sulphuric acid process was developed on a commercial scale in the 1890's and produces high purity acid of any desired concentration. About 98 per cent of the sulphuric acid produced in the United Kingdom in 1971 was manufactured by this process, mainly using crude sulphur: of the 61 units operating the contact process in England and Wales, crude sulphur was the basis in 40 units, pyrites in 5, anhydrite in 7, spent oxide in 2 and miscellaneous raw materials in 7 units. A mixture of SO_2 and air is heated to 400 to 450°C and fed into a converter, where it is exposed to a solid platinum or, more recently, vanadium pentoxide catalyst. After the oxidation of about 95 per cent of the SO_2, the resultant sulphur trioxide (SO_3) meets a stream of 100 per cent sulphuric acid in an absorber tower. The solution of SO_3 in sulphuric acid is known as *oleum,* which is either left intact and marketed on the basis of the percentage of SO_3 present, or diluted with water to provide different concentrations of sulphuric acid. The contact process may also be used to fortify spent acid and the more dilute acids produced in a lead chamber plant.

The older contact sulphuric acid plants in the United Kingdom meet a standard set by the Alkali Inspectorate of 98 per cent efficiency. However, several contact units within the range of about 250 to 750 tonnes of sulphuric acid per day have been built which employ a double absorption technique introduced by the Bayer group in Germany and further developed in the USA. The technique has an efficiency of 99.5 per cent which the sulphuric acid industry in the United Kingdom has accepted as the standard for new contact plants burning crude sulphur. At Billingham, two such units together capable of producing 300,000 tonnes of acid a year came on stream in 1971, and a 200,000 tonnes a year plant has been installed at Avonmouth. A 250,000 tonnes per annum plant has come into operation at the Rocksavage works, near Runcorn, and another double contact plant with a capacity of 160,000 tonnes per annum was built in 1972 at Greenfield in North Wales.

The *lead chamber* sulphuric acid process derives its name from the large chambers lined with sheet lead in which the same reaction takes place as in the contact process, but nitrogen dioxide is used as a catalyst. Unless a pure raw material such as crude sulphur is used, the sulphuric acid produced is relatively impure and generally contains 62 or 70 per cent H_2SO_4, a concentration that is suitable for the manufacture of phosphatic fertilisers. Usually three or four chambers are employed through which the SO_2 gas is passed until it has all combined to form sulphuric acid. Although it produces sulphuric acid more cheaply, it has proved difficult to regulate the concentration of sulphuric acid leaving the chambers, and since lead is attacked by very strong sulphuric acid, higher concentrations of acid have to be avoided if the chambers are to be used over a long period of time. There were only four lead chamber sulphuric acid plants in operation in England and Wales at the end of 1971.

Production

Anhydrite has been produced in the United Kingdom for many years for the manufacture of both sulphuric acid and ammonium sulphate. It accounted for about 11 per cent of the sulphuric acid manufactured in the United Kingdom in 1972. Relatively small amounts of sulphur are also made available from sulphide smelter gases, oil refineries and spent oxide (Table 2). Together, these sources provided less than one-fifth of the 1,360,000 tonnes of sulphur or sulphur equivalent estimated to have been consumed in the United Kingdom in 1972.

Table 2 United Kingdom: Estimated domestic production of sulphur and sulphur-bearing raw materials, 1968–1972

Thousand tonnes sulphur or sulphur equivalent

Source	1968	1969	1970	1971	1972
Anhydrite	400	378	311	225	163
Zinc concentrates	97	97	87	85	32
Recovered from oil refineries	38	40	32	44	41
Spent oxide	68	54	35	18	5
Total	603	569	465	372	241

Source: Institute of Geological Sciences, based on statistics published by the Department of Trade and Industry and the National Sulphuric Acid Association.

Anhydrite

The United Kingdom is a major producer of anhydrite, estimated output amounting to 778,000 tonnes in 1972, almost all of which was consumed in sulphuric acid manufacture, as shown in Table 3.

Table 3 United Kingdom: Estimated production of anhydrite, 1963–1972

Year	*Total* *Thousand tonnes*	*Used for sulphuric acid* *Thousand tonnes*
1963	2,126	857
1964	2,073	957
1965	1,862	992
1966	1,744	995
1967	1,760	1,154
1968	1,907	1,278
1969	1,801	1,229
1970	1,479	1,204
1971	1,070	1,051
1972	778	741

Source: Department of Trade and Industry.

Anhydrite was produced from 1923 until 1926 and has been mined continuously since March 1928, when the Billingham mine was opened by Imperial Chemical Industries Limited. About 40 million tonnes of anhydrite has been produced in the United Kingdom since then, the Billingham mine having provided about 30 million tonnes, including virtually all the anhydrite produced before 1955. Substantial increases in production took place after 1955, when new anhydrite mines came into operation in northern England and sulphuric acid capacity at Billingham was raised from 101,000 to 178,000 tonnes per annum, total output reaching a maximum of 2,126,000 tonnes in 1963. Additional sulphuric acid plant using anhydrite was installed in 1966 and 1967 and in 1968 nearly 21 per cent of the sulphuric acid produced in the United Kingdom was made from anhydrite. Production of anhydrite has declined substantially since 1969 and the Billingham mine was closed in August, 1971. The production of sulphuric acid from anhydrite at Billingham ended in September, 1971, and the three anhydrite kilns and one sulphur-burning unit were replaced by plants burning crude sulphur. During their life, these kilns produced more than 5½ million tonnes of sulphuric acid. The anhydrite-based sulphuric acid plant at Widnes closed in March, 1973, and at Whitehaven two of the five kilns which together had a sulphuric acid capacity of 400,000 tonnes per annum have also been replaced by a unit using crude sulphur.

Prior to the 1950's all the anhydrite was produced at Billingham for the manufacture of ammonium sulphate. However, this fertiliser has since declined rapidly in importance and its production from anhydrite ceased at Billingham in April,1971. During the early 1960's, the United Kingdom was a major world producer of ammonium sulphate, producing a maximum of just over 1 million tonnes in 1963.

Sulphide concentrates (excluding pyrites)

Sulphur in the form of SO_2 in smelter exit gases is produced in the United Kingdom at Avonmouth, where a plant capable of producing some 200,000 tonnes of sulphuric acid a year came into operation in 1967. Exit gases containing about 6 per cent SO_2 from the Imperial Smelting Furnace No 4 are used to make sulphuric acid for the production of phosphoric and hydrofluoric acids.

A sulphuric acid plant at Swansea Vale, Llansamlet,which produces between 100,000 and 120,000 tonnes a year, came into operation in the 1920's using ferrous sulphate, spent oxide and imported iron pyrites. Exit gases were used after the commissioning of Imperial Smelting Furnace No 3 in 1960. However, the furnace was shut down in 1971 in order to concentrate smelter operation in the Avonmouth complex, since when acid has been produced at Swansea Vale from imported crude sulphur. Both the Avonmouth and Swansea Vale sulphuric acid plants are operated by ISC Chemicals Limited, a subsidiary of Commonwealth Smelting Europe Limited.

According to statistics published by the National Sulphuric Acid Association Limited, some 4¼ million tonnes of zinc concentrates was utilised (indirectly) in the manufacture of sulphuric acid during the period 1950-1972. Consumption of zinc concentrates fell from about 380,000 tonnes in 1970 to only 141,199 tonnes in 1972. The average sulphur content of zinc concentrates used in the manufacture of sulphuric acid is about 29 per cent.

Hydrocarbons

Recovery of sulphur and sulphur compounds from some products and intermediates during oil refining is a post-war development in the United Kingdom. More than 99 million tonnes of crude petroleum were refined in England and Wales in 1972. During refining some gas streams have a relatively high concentration of H_2S and sulphur can be recovered. Low sulphur gas streams are usually used as fuel for furnaces, where the H_2S is converted to SO_2 and dispersed with other products of combustion. Sulphur recovery is variable (Table 2) and in 1972 was taking place at 7 of the 19 refineries in England and Wales at an average rate of about 128 tonnes per day. Most of the sulphur is recovered to meet market requirements for the refinery products, but it is also recovered to reduce air pollution from refineries and is encouraged by the Alkali Inspectorate. The installation of sulphur recovery systems is a requirement at new refineries.

North Sea natural gas is virtually sulphur-free, although gas from the Hewett field contains about 0.053 per cent H_2S and it is planned to produce an average of about 6 tonnes of sulphur a day at a plant at Bacton in Norfolk. Substantial reserves of natural gas containing about 0.05 per cent H_2S are being developed near Lockton, Yorkshire, and plant capable of recovering about $^2/_3$ tonne of sulphur per million cubic metres of gas processed has been installed; some sulphur was recovered for sale during 1972.

Spent oxide

More than 4.5 million tonnes of spent oxide containing between 2 and 3 million tonnes of sulphur is estimated to have been used during the past 30 years for the manufacture of sulphuric acid. Production has fallen very substantially since 1967 (Table 2) due to the decline in coal carbonisation and the use of natural gas from the North Sea. Consumption of spent oxide amounted to 70,651 tonnes in 1970 and to only 38,613 tonnes in 1972. The higher grades are normally reserved for the domestic sulphuric acid industry, but small quantities of lower grade material have been made available for export. Spent oxide from gas works was first used by the chemical industry in the United Kingdom in 1870.

It is estimated that up to 1975, and probably for some time after, between 20 million and 25 million tonnes a year of coal will be carbonised in coke ovens for use by steel works; if all the gas were purified about 200,000 tonnes a year of sulphur would be available for recovery. However, using existing processes the economics of recovery are unattractive except in isolated circumstances. The approximate amounts of sulphur recoverable from coke-oven gas produced by the British Steel Corporation in South Wales, for example, are shown in Fig 4.

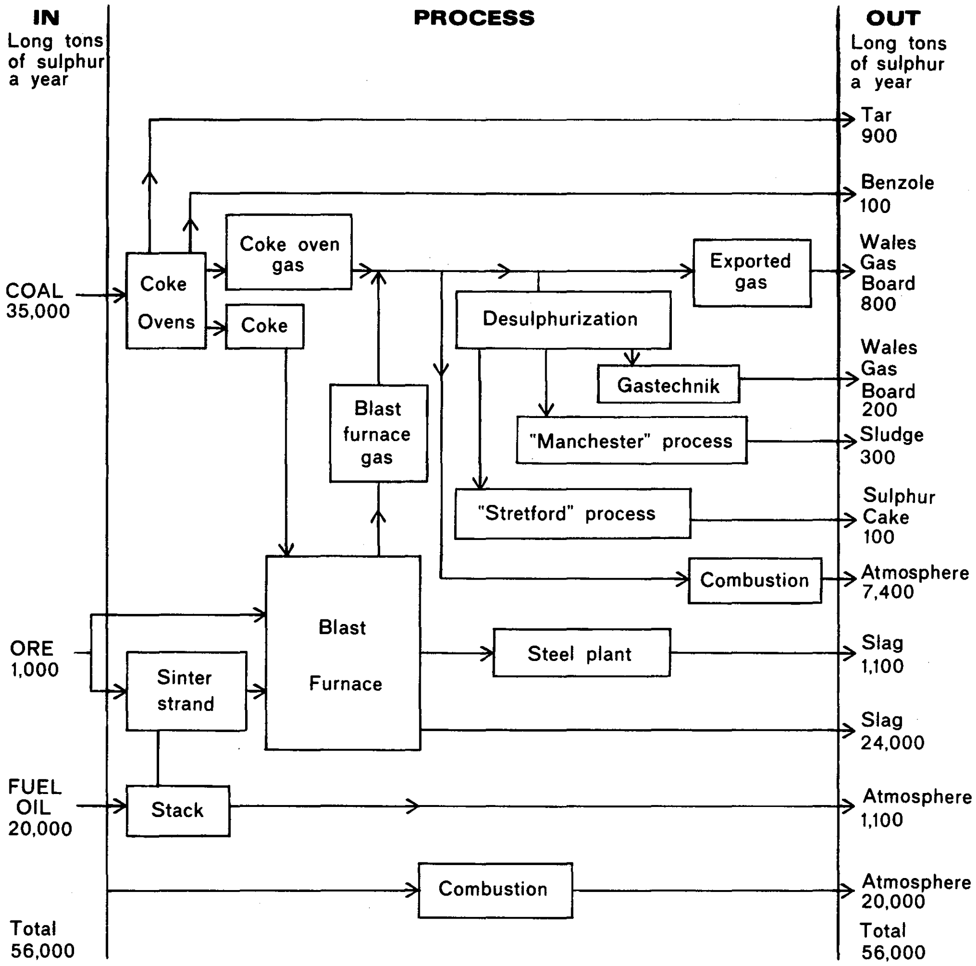

Fig 4 Sulphur balance arising from coal, ore and fuel oil used in steel manufacture

Ferrous sulphate

Small tonnages of sulphuric acid are derived from ferrous sulphate produced as waste pickle liquor in steel making. However, the quantities of ferrous sulphate available for acid manufacture is likely to decrease since at least one steel works, the Margam works at Port Talbot,now uses hydrochloric acid for pickling. The approximate amounts of sulphuric acid used by the British Steel Corporation in South Wales in steel pickling are shown in Fig 5.

Substantial quantities of hydrated ferrous sulphate (copperas) are produced in the manufacture of titanium oxide pigment, each tonne of pigment giving rise to about 3 to 4 tonnes of ferrous sulphate and about 5 tonnes of dilute sulphuric acid, including wash water. As far as is known, however, the ferrous sulphate is not utilised.

Pyrites

Pyrites has been produced from metalliferous veins in various parts of the United Kingdom, chiefly as a by-product, and at coal washing plants, but no production has been recorded since 1959. Commercial production of pyrites appears to have commenced about the middle of the 19th century and was mainly confined to the succeeding 25 to 30 years. Total recorded output is between 700,000 and 800,000 tonnes of pyrites, equivalent to at least 356,000 tonnes of sulphur.

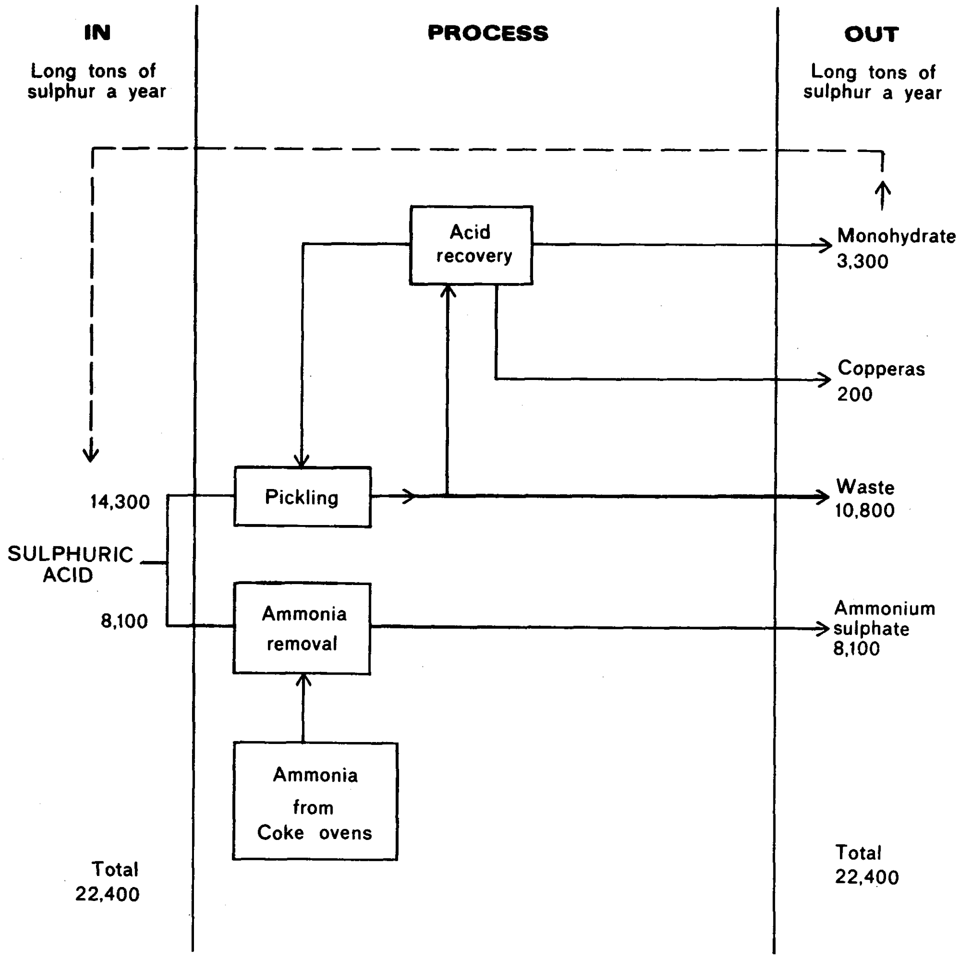

Fig 5 Sulphur balance in the use of sulphuric acid in steel manufacture

Pyrites was recovered from most of the mines of south-west England, usually as a by-product, but some small mines produced larger tonnages of pyrites than of other minerals. Between 1850 and 1875 recorded production from about 70 different mines amounted to some 150,000 tonnes. The largest outputs came from Wheal Jane and West Wheal Jane east of St Day, Cornwall, which together produced over 61,000 tonnes. Small quantities of pyrites nodules derived from the London Clay were obtained by hand picking on the foreshore of the Isle of Sheppey, Kent, from 1875 to 1914.

The only mine in Wales to have been worked specifically as a source of pyrites is Cae Coch, near Trefriw in the Conway Valley, Caernarvonshire. Between 1826 and 1835 the mine, which was owned by William Hill of Liverpool, supplied about 3,600 tonnes of pyrites, which was brought to Liverpool by sea for experiments in sulphuric acid manufacture. Between 1860 and 1875 approximately 91,000 tonnes of ore was produced; about 16,000 tonnes was produced in the latter half of the First World War. Most of the output in Scotland appears to have been in the form of 'coal brasses', obtained chiefly from the Dumbartonshire coalfields. Pyrite-bearing slates were worked for pyrites in Argyllshire for more than 200 years

Most of the pyrites produced since the First World War has been recovered in coal washing plants. Initially up to about 10,000 tonnes a year of hand-picked lump pyrites was produced, declining to some 4,000 or 5,000 tonnes a year before the Second World War, when annual output rose to 9,000 tonnes and, additionally, about 71,000 tonnes of 'fines' were produced. Since the war, output of pyrites has steadily declined, amounting to about 5,000 tonnes of 'fines' and 3,000 tonnes lump pyrites a year until production ceased in the 1950's, when recovery became uneconomic.

World production and trade

World production of both elemental sulphur and other forms of sulphur reached about 45.5 million tonnes in 1972 compared with about 6.8 million tonnes in 1929, representing an average annual rate of increase of 4.5 per cent. More than three-quarters was produced in the USA, the USSR, Canada, Poland, Japan, France and Mexico, as shown in Table 4.

The Frasch mines of Louisiana and Texas have been the major sources of crude sulphur in the world since 1913 and these, together with the Frasch mines of Mexico which came into operation in 1954, produced about 8.3 million tonnes in 1971. Poland, which became a major world producer in the late 1960's, has both opencast and Frasch mines. Frasch sulphur production in the USA and Mexico declined in 1970, when for the first time world production of recovered sulphur in countries outside the Communist Bloc exceeded primary sulphur production.

The bulk of the recovered sulphur is obtained from H_2S occurring in natural gas deposits in Canada, France and the USA. Production of recovered sulphur began in the USA in the early 1940's, after the discovery of sour natural gas fields in south-west Arkansas: it is also obtained from natural gas in Wyoming and Texas. Canada became a producer in 1951, with the development of the important gas fields of Alberta, while in south-west France production began in 1957 from the major Lacq gas field. In Iran, production began in 1971.

Some 94 per cent, or about 7.7 million tonnes, of total crude sulphur exports (derived from Frasch and recovered sulphur) was provided by the USA, Canada, Mexico, France and Poland in 1971, largely to markets in western Europe (Table 5). Canada became the largest exporter of crude sulphur for the first time in 1968.

Total world production of pyrites was estimated at 22.1 million tonnes in 1971, equivalent to about 10.3 million tonnes of sulphur, the USSR and Japan being the largest producers. The most important sources of supply in Europe are Spain, Italy and the Federal Republic of Germany, while Cyprus, Norway, Portugal and Finland are also established producers. Exports from the USSR in 1971 amounted to about 1.8 million tonnes, of which over one million tonnes was shipped to western Europe, chiefly to Italy and Federal Germany, the world's largest importers of pyrites (Table 6).

Table 4 World production of sulphur, 1968–1972

Millions of tonnes sulphur or sulphur content

Country and description	1968	1969	1970	1971	1972
Elemental Sulphur (native or recovered)					
USA	9.0	8.7	8.6	8.8	9.3
Canada	3.2	3.9	4.4	4.7	6.9
Poland	1.3	1.9	2.7	2.8	3.1
France	1.6	1.7	2.0	1.8	1.7
USSR	1.6	1.7	1.7	2.2	2.4
Mexico	1.7	1.7	1.4	1.2	0.9
Japan	0.3	0.3	0.3	0.4	0.5
Others	1.1	1.2	1.8	1.8	2.2
Total	19.8	21.1	22.9	23.7	27.0
Non-elemental sulphur (contained in pyrites or recovered as acid, etc., from other sources)					
USSR *(a)*	3.8	3.9	4.8	5.0	5.0
Japan *(b)*	2.3	2.4	2.5	2.3	2.1
USA	1.5	1.6	1.7	1.6	1.7
Spain *(a)*	1.2	1.3	1.5	1.3	1.1
China *(a)*	0.8	0.9	0.9	0.9	0.9
Italy *(a)*	0.8	0.8	0.9	0.9	0.8
Canada	0.7	0.7	0.8	0.8	0.8
Germany (Federal)	0.5	0.6	0.6	0.6	0.6
Norway *(a)*	0.4	0.4	0.4	0.4	0.4
Finland	0.3	0.3	0.4	0.4	0.4
Cyprus (pyrites)	0.5	0.4	0.4	0.4	0.3
UK *(c)*	0.5	0.5	0.4	0.3	0.2
South Africa *(a)*	0.3	0.3	0.3	0.3	0.3
Germany (East)	0.3	0.3	0.3	0.3	0.3
Portugal *(a)*	0.3	0.2	0.3	0.2	0.2
France	0.2	0.2	0.2	0.2	0.2
Poland	0.3	0.2	0.2	0.2	0.2
North Korea *(a)*	0.2	0.2	0.2	0.2	0.2
Others	2.2	2.5	2.0	2.7	2.8
Total	17.1	17.7	19.2	19.0	18.5
Total (all forms)	36.9	38.8	42.1	42.7	45.5

(a) Chiefly pyrites *(b)* chiefly pyrites and pyrrhotite *(c)* chiefly anhydrite

Source: Institute of Geological Sciences.
United States Bureau of Mines.
The British Sulphur Corporation Limited.

Table 5 World exports of crude sulphur, by major suppliers, 1971

Thousand tonnes

To:	CANADA	POLAND	USA	FRANCE	MEXICO
Europe	558	1,483	1,098	714	143
Africa	3	201	86	163	
North America	915		38		444
South & Central America	134	156	242	43	68
Asia	414	213	12	28	28
Australasia	378	11	80		
World Total	2,402	2,064	1,556	948	683

Source: Institute of Geological Sciences, based on trade returns of individual exporting countries.

Table 6 World exports of pyrites, by major suppliers,

Thousand tonnes

To:	USSR	SPAIN	CYPRUS	NORWAY	PORTUGAL
United Kingdom	36	10	71	47	
Belgium		201	11		141
Denmark		131			46
France	26	92	154		
Federal Germany	416	466	10	409	
Italy	534		122		
Netherlands			181		
Greece		9			
Sweden				89	
Czechoslovakia	134				
Germany (East)	174				
Hungary	111				
Egypt		27	35		
Others	369 *(a)*		28		
Total	1,800	936 *(b)*	612 *(c)*	545	187

(a) Includes exports of 179,000 tonnes to Yugoslavia

(b) Includes exports of 180,000 tonnes of cupreous iron pyrites: Denmark, 3,000 tonnes; France, 20,000 tonnes; and the Federal Republic of Germany, 157,000 tonnes

(c) Does not include exports of cupreous pyrites, which in 1971 totalled 74,500 tonnes

Source: Institute of Geological Sciences, based on trade returns of individual exporting countries.

Many industrialised countries also utilise sulphur made available from sources other than crude sulphur and pyrites. The United States is the largest producer of sulphuric acid from smelter gases, for example, and also uses large quantities of H_2S from oil refinery gases for acid manufacture. Anhydrite is used in the manufacture of sulphuric acid in the United Kingdom and Austria; gypsum is mined in Italy, India, Turkey and Pakistan for the production of ammonium sulphate.

Significant quantities of sulphur are being produced by desulphurising fuel oil. The first large scale plant came into operation in Japan in 1967, with a capacity of about 500,000 tonnes a year. The Japan Sulphur Export Company was formed in 1970 to market the anticipated surplus sulphur produced, but only very limited quantities of recovered sulphur have been exported because of the contraction of the domestic sulphur mining industry. Plants are operating on a commercial scale also in the Caribbean, Kuwait and Sweden. Spent oxide is used in the manufacture of sulphuric acid chiefly in western Europe and in Japan although production from this source has declined substantially. As far as is known Sweden is the only country to have produced significant quantities of sulphur from oil shale, nearly 5,244 tonnes being produced in 1971. At Fort McMurray in Alberta a sulphur recovery plant capable of producing about 110,000 tonnes a year was installed in 1967 by one of the oil companies developing the Athabasca tar sands. Some 61,000 tonnes of sulphur was recovered in 1971.

United Kingdom trade and consumption

The United Kingdom is a major importer of sulphur, about four-fifths of annual sulphur requirements being met by imports of crude sulphur, chiefly from France, Poland, Mexico, Canada and the USA, and of pyrites, which traditionally has been supplied by Cyprus, and in recent years also by Norway, Sweden and the USSR. Sulphur requirements for most consumers in the sulphuric acid industry are obtained through the National Sulphuric Acid Association Limited in London, which was formed in 1919. Imports of crude sulphur and unroasted pyrites for the period 1948-1972 are shown in Table 7. The countries of origin of these imports for the period 1968-1972 are shown in Table 8.

Stocks of pyrites were acquired by the British Government during the Korean War for strategic purposes. Deliveries to sulphuric acid works in the United Kingdom commenced in 1958/59 and continued until stocks became exhausted in October 1969. Deliveries were as follows:

	Tonnes
1958/59	32,192
1959/60	55,628
1960/61	65,421
1961/62	55,787
1962/63	51,250
1963/64	26,948
1964/65	13,500
1965/66	10,875
1966/67	13,138
1967/68	11,647
1968/69	7,691

Source: The National Sulphuric Acid Association Limited.

Table 7 United Kingdom: Imports of sulphur and unroasted pyrites, 1948-1972

	Sulphur		*Sulphur wastes and residues*		*Pyrites*		*Total value of UK import*
	Quantity	*Value cif*	*Quantity*	*Value cif*	*Quantity*	*Value cif*	
	tonnes	*£*	*tonnes*	*£*	*tonnes*	*£*	*£*
1948	354,186	2,956,471	not separately specified		216,218	829,598	3,786,069
1949	399,229	3,405,393			234,019	890,408	4,295,801
1950	446,322	4,395,752			194,711	835,667	5,231,419
1951	383,369	6,095,717			353,268	2,303,177	8,398,894
1952	413,713	5,687,713			513,207	3,553,685	9,241,398
1953	199,903	2,552,893			391,313	2,602,156	5,155,049
1954	380,636	5,003,453			609,215	4,077,258	9,080,711
1955	364,455	5,376,964			507,208	3,658,198	9,035,162
1956	358,197	5,352,598	12,324	126,289	390,825	2,884,029	8,362,916
1957	330,939	4,793,617	13,488	136,025	362,556	2,534,333	7,463,975
1958	332,899	3,713,154	9,702	80,921	249,081	1,325,182	5,119,257
1959	383,502	4,026,126	15,003	100,597	216,873	1,044,441	5,171,164
1960	494,895	5,060,657	13,748	93,707	274,314	1,228,320	6,382,684
1961	504,197	4,959,487	20,401	128,194	272,015	1,198,225	6,285,906
1962	503,738	5,063,619	17,259	130,675	286,045	1,171,391	6,365,685
1963	551,773	4,997,647	12,956	115,908	203,538	818,132	5,931,687
1964	721,040	6,237,708	–	1	288,868	1,186,298	7,424,007
1965	798,719	8,207,471	10,108	108,453	227,940	1,009,696	9,325,620
1966	769,169	11,582,363	466	1,477	263,393	1,423,684	13,007,523
1967	714,203	11,542,632	15,606	264,213	245,629	1,300,383	13,107,228
1968	781,370	14,925,977	included with "sulphur"		219,805	1,407,477	16,334,454
1969	742,208	12,808,918			220,706	1,347,640	14,156,558
1970	817,562	8,740,351			169,904	1,039,085	9,779,436
1971	962,017	9,759,893			213,799	1,167,586	10,927,479
1972 *(p)*	1,038,641	10,298,000			132,502	694,000	10,992,000

(p) Provisional figures

Source: HM Customs and Excise

Table 8 United Kingdom: Imports of crude sulphur and unroasted pyrites, by countries, 1968–1972

Tonnes

	1968	1968	1970	1971	1972 *(p)*
Sulphur					
France	278,508	235,524	275,341	338,611	369,672
Poland	61,811	163,503	196,022	264,436	290,961
Mexico	310,845	129,474	97,459	202,623	174,126
Canada	9,539	17,928	53,630	50,628	101,119
USA	114,315	173,107	118,499	45,118	68,981
Netherlands	5,566	21,626	76,121	55,228	29,825
Germany (Federal) *(a)*	784	663	489	437	*n.a.*
Other Countries	1	383	1	4,936	3,977 *(b)*
Total	781,370	742,208	817,562	962,017	1,038,641
Unroasted Pyrites					
Cyprus	106,600	93,860	95,283	82,352	47,339
USSR	35,312	44,209	16,323	33,881	39,266
Norway	4,197	11,078	16,970	49,975	25,283
Sweden	52,163	47,830	31,051	40,852	10,976
Spain	21,367	23,515	9,464	6,470	*n.a.*
Other Countries	166	212	813	269	9,638 *(p)*
Total	219,805	220,706	169,904	213,799	132,502

n.a. Information not available
(p) Provisional figures
(a) Special grades for rubber manufacture
(b) Includes Federal Republic of Germany, if any
(c) Includes Spain, if any

Source: HM Customs and Excise.

In addition to imports of crude sulphur and pyrites, sulphuric acid has been imported into the United Kingdom since 1967, notably from the Federal Republic of Germany, the Netherlands, Sweden and Norway; imports of sulphuric acid amounted to nearly 150,000 tonnes in 1972. In the same year, about 180,000 tonnes of sulphuric acid were recovered in the United Kingdom (Table 9).

Table 9 United Kingdom: Imports and recovery of sulphuric acid, 1968–1972

	Imported	Recovered
	Tonnes	
1968	190,880	126,855
1969	320,333	148,120
1970	276,614	151,942
1971	211,217	157,903
1972	149,984	180,378

Source: The National Sulphuric Acid Association Limited.

Imports of crude sulphur and pyrites accounted for about four-fifths of the 1.36 million tonnes of sulphur equivalent estimated to have been consumed in the United Kingdom in 1972. Of this total, 1,211,000 tonnes was consumed in the manufacture of sulphuric acid, as shown in Table 10.

Table 10 United Kingdom: Estimated consumption of sulphur, 1972

	Thousand tonnes S
For sulphuric acid manufacture	
Elemental sulphur *(a)*	929
Anhydrite	156
Pyrites	66
Zinc concentrates	41
Spent oxide	19
Total	1,211
Other uses	
Elemental sulphur	141
Anhydrite	7
Total	148
Total (all forms)	1,359

(a) Including sulphur recovered from petroleum refining and the sulphur content of hydrogen sulphide, ferrous sulphate and filter cake

Source: Institute of Geological Sciences, based on statistics compiled by the Department of Trade and Industry and the National Sulphuric Acid Association Limited.

Demand trends

Sulphur is an essential raw material, the demand for which, particularly in sulphuric acid manufacture will undoubtedly continue to rise. In the United Kingdom there has been a marked increase in the consumption of sulphur since 1963, although there were fluctuations in the late 1960's, due to a decrease in the rate of growth of the phosphatic fertiliser industry. There has also been an increase in the consumption of sulphuric acid by each of the major acid-consuming industries, (*see* Fig 2), with the notable exception of ammonium sulphate production. Total consumption of sulphuric acid in the United Kingdom amounted to 3,814,504 tonnes in 1971; in that year the consumption of sulphuric acid in the manufacture of phosphatic fertilisers increased by 7 per cent. Consumption amounted to 3,819,611 tonnes in 1972.

In 1971, at a meeting sponsored by the International Superphosphate and Compound Manufacturers' Association Limited and The Sulphur Institute, it was suggested that total Western World consumption of sulphur, based on existing traditional use, would grow at the rate of 4.4 per cent a year to 35.6 million tonnes in 1975. Taking into account possible new uses, the additional sulphur consumption would be 750,000 tonnes. An important factor in determining the demand for sulphur is the corresponding demand for phosphatic fertilisers. For example, the shortage of sulphur experienced between 1964 and 1968 was due primarily to the sudden and remarkable growth in demand by the fertiliser industry at a rate of over 10 per cent per annum and the consequent increase in demand for sulphuric acid.

One future problem likely to face the sulphur industry in the anticipated need to create new market outlets for the large tonnages of surplus sulphur that are foreseen. The Sulphur Institute, which is supported by various producers of Frasch and recovered sulphur and pyrites, is prominent among a number of organisations carrying out research. In Canada, research is being carried out by the Research Council of Alberta and the Alberta Sulphur Research Limited. One significant development is the possible use of sulphur as an extender of asphalt in road construction. The preparation of sulphur foams, sulphur concretes and sulphur-based paints is also being investigated (*see* page 11). The National Sulphuric Acid Association forecast in 1972 that the demand for elemental sulphur was likely to rise above the historical growth rate of 4 to 5 per cent a year for the next few years, with elemental sulphur acquiring a greater share of the world sulphur market while low prices prevail, at the expense of other sulphur-bearing raw materials, primarily pyrites, gypsum and anhydrite.

The demand for sulphur can be reduced by using alternatives to sulphuric acid. For example, in some countries nitrophosphates made with nitric acid are important. The nitrophosphate process involves a high level of capital expenditure, however, and limits the range of fertilisers produced, unless phosphoric acid is also added. There is a tendency to utilise increasing quantities of hydrochloric acid instead of sulphuric acid in steel pickling, while the consumption of sulphuric acid for pigment production can be reduced by the use of the alternative chloride route. In general, regeneration of sulphuric acid from the by-product ferrous sulphate (copperas) is not economic. Processes for the manufacture of phosphoric acid using acid other than sulphuric acid are available but are employed only on a limited scale at present.

Replacement of crude sulphur imports

Periodic world shortages of crude sulphur and accompanying high prices have in the past prompted a number of countries to re-evaluate domestic resources of sulphur-bearing raw materials. However, while abundant supplies of low-cost crude sulphur are available on the world market, such sources of sulphur as anhydrite or gypsum are no longer promising. In the United Kingdom the sulphur crisis in the early 1950's encouraged the increased use of anhydrite for the manufacture of acid. As a result, the percentage of sulphuric acid made from anhydrite rose markedly from 5.5 per cent in 1950 to 11 per cent in 1955, reaching 21 per cent in 1968 and falling with the accompanying decline in anhydrite production to 11.4 per cent in 1972.

Several sulphuric acid projects were considered in other countries during the late 1960's which might have been brought into commercial operation if the local source, principally in the form of pyrites or anhydrite and gypsum, could have been utilised more economically in the absence of a plentiful supply of crude sulphur on the world market. One of the most interesting projects involved the construction of the Rock House plant north-west of Van Horn in western Texas which was completed by the Elcor Chemical Corporation in 1968. The plant was to use locally mined gypsum and had a planned annual capacity of about 350,000 tonnes of elemental sulphur which, according to one report, could be recovered for about $25 per short ton (£11.48 per tonne) assuming a fuel cost of 20 cents (8p) per million Btu, and a price of $2 per short ton (92p per tonne) of $CaSO_4$. It was claimed that the operation would be profitable even if the price of elemental sulphur fell to £12.3 per tonne. However, the project was overtaken by the world slump in sulphur prices and the plant was closed in November, 1970, without achieving commercial production.

Phosphogypsum has attracted interest in some countries where natural gypsum (or anhydrite) of good quality is not obtainable locally or where there is a particular problem in the disposal of this waste material. It is used for sulphuric acid manufacture on a commercial scale in South Africa at Phalaborwa in northern Transvaal, in a plant which has a capacity of about 108,000 tonnes of sulphuric acid per annum. Phosphogypsum has been tested in East Germany for the manufacture of sulphuric acid and cement clinker since about 1968 but there has been no commercial production, as far as is known. Phosphogypsum is used also in the manufacture of ammonium sulphate in Japan; very small quantities have been used for the same purpose in India to supplement supplies of natural gypsum.

Production of sulphuric acid from crude sulphur is technically the cleanest and most attractive process in terms of ease of operation and efficiency of recovery. Comparing crude sulphur with pyrites,the two most decisive factors are the price per unit sulphur, bearing in mind any credit which may arise from the sale of the metal-bearing cinders in the case of pyrites, and differences in capital costs, which for plant using pyrites, including roasters and gas cleaning equipment, is up to three times that of one based on crude sulphur.

The economics of acid production from anhydrite or gypsum depends on plant location in relation to raw materials, the considerable capital investment involved, the cost and availability of fuels, as well as the markets for the co-product cement which must be sold within a reasonable radius of production. In addition the process is more complex, needing more precise control, and must be run continuously and near or at maximum capacity. Operating costs are also substantially higher for a plant using anhydrite in place of crude sulphur. The capital cost of a sulphuric acid plant of 600 tonnes per day capacity and based on anhydrite was about £5 million in 1970, compared with a cost of £1.1 million for a plant of the same capacity using crude sulphur. Sulphur would have to be priced at over £20 per tonne for the process to become competitive, with a breakeven sulphur price of about £22.50 per tonne. If phosphogypsum is used the capital cost is approximately 20 per cent higher than in the case of anhydrite but this is partly offset by lower raw material costs.

Industry

Anhydrite is the only naturally-occurring source of sulphur mined at present in the United Kingdom. It is produced by Albright and Wilson Limited (Marchon Division) at Sandwith in Cumberland, where two anhydrite beds separated by dolomitic marl are worked, the hard, brittle, anhydrite being broken up by means of percussion drilling and the use of high-velocity explosives. After crushing and screening, a belt conveyor carries the anhydrite to the surface at the rate of up to 450 tonnes an hour. Anhydrite was produced by British Gypsum Limited at the Long Meg mine in Cumberland until March, 1973 and on a limited scale at Newbiggin, Westmorland. Until 1971 anhydrite was also mined by Imperial Chemical Industries Limited (Agricultural Division) at Billingham, Co Durham, the largest anhydrite mine in the world. At all these mines anhydrite has been worked underground by pillar and stall methods, using trackless mining. The output from the Sandwith mine is consumed captively, as was that produced at Billingham, but anhydrite produced at Long Meg was transported by rail to a sulphuric acid plant operated by the United Sulphuric Acid Corporation Limited at Widnes in Lancashire, a distance of approximately 160 km. The Corporation was formed in 1951 as a co-operative venture between eleven participants to manufacture sulphuric acid from indigenous raw materials, particularly anhydrite, because of shortages of Frasch sulphur from the Mexican Gulf induced by the Korean war.

The United Kingdom sulphuric acid industry is one of major world importance, ranking sixth after the USA, the USSR, Japan, the Federal Republic of Germany and France in 1972, when the United Kingdom produced 3.4 million tonnes of sulphuric acid (Table 11).

Table 11 World production of sulphuric acid, by major producing countries, 1968-1972

Thousand tonnes 100 per cent H_2SO_4

	1968	1969	1970	1971	1972*(p)*
United States	25,906	26,061	26,448	26,568	27,264
USSR	10,166	10,668	12,058	12,775	13,692
Japan	6,591	6,759	6,925	6,660	6,714
Germany (Federal)	4,210	4,481	4,435	4,388	4,740
France	3,349	3,527	3,682	3,923	4,116
United Kingdom	3,335	3,287	3,352	3,459	3,449
Italy	3,313	3,354	3,330	3,106	3,115
Spain	2,067	2,148	2,076	1,896	2,490
Total	58,937	60,396	62,308	62,694	65,580
World Total	84,270	86,959	91,152	94,302	98,000

(p) Provisional figures

Source: Compiled by the Institute of Geological Sciences, chiefly from data published by the United Nations and the British Sulphur Corporation Limited.

There were about 47 sulphuric acid works in the United Kingdom in 1971, those with a capacity of 50,000 tonnes of more a year being shown in Fig 6. Most works are at or near major ports, notably Immingham and Manchester, reflecting the dependence of the domestic acid industry on imported raw materials. On 31st December,1971, the 24 member companies of the National Sulphuric Acid Association Limited accounted for 99.7 per cent of the sulphuric acid manufacturing capacity in the United Kingdom and Eire amounting to some 4.1 million tonnes. About three-quarters of this capacity comprises works operated by Imperial Chemical Industries Limited, and its subsidiary Scottish Agricultural Industries Limited formed in 1928, ISC Chemicals Limited (a subsidiary of Commonwealth Smelting Europe Limited),Laporte Industries Limited, Albright and Wilson Limited, Fisons Limited, British Titan Products Company Limited and Courtaulds Limited. Works with a capacity ranging from 100,000 to 200,000 tonnes per annum are in operation at Avonmouth, Billingham, Immingham, Severnside, Stallingborough, Stratford (London), Whitehaven and Widnes.

The Stratford works which is operated by Berk Spencer Acids Limited (a subsidiary of the Steetley Company Limited) is probably the only one using significant tonnages of sulphur from oil refineries, sulphuric acid manufacture being based partly on liquid sulphur from the Esso refinery at Fawley,

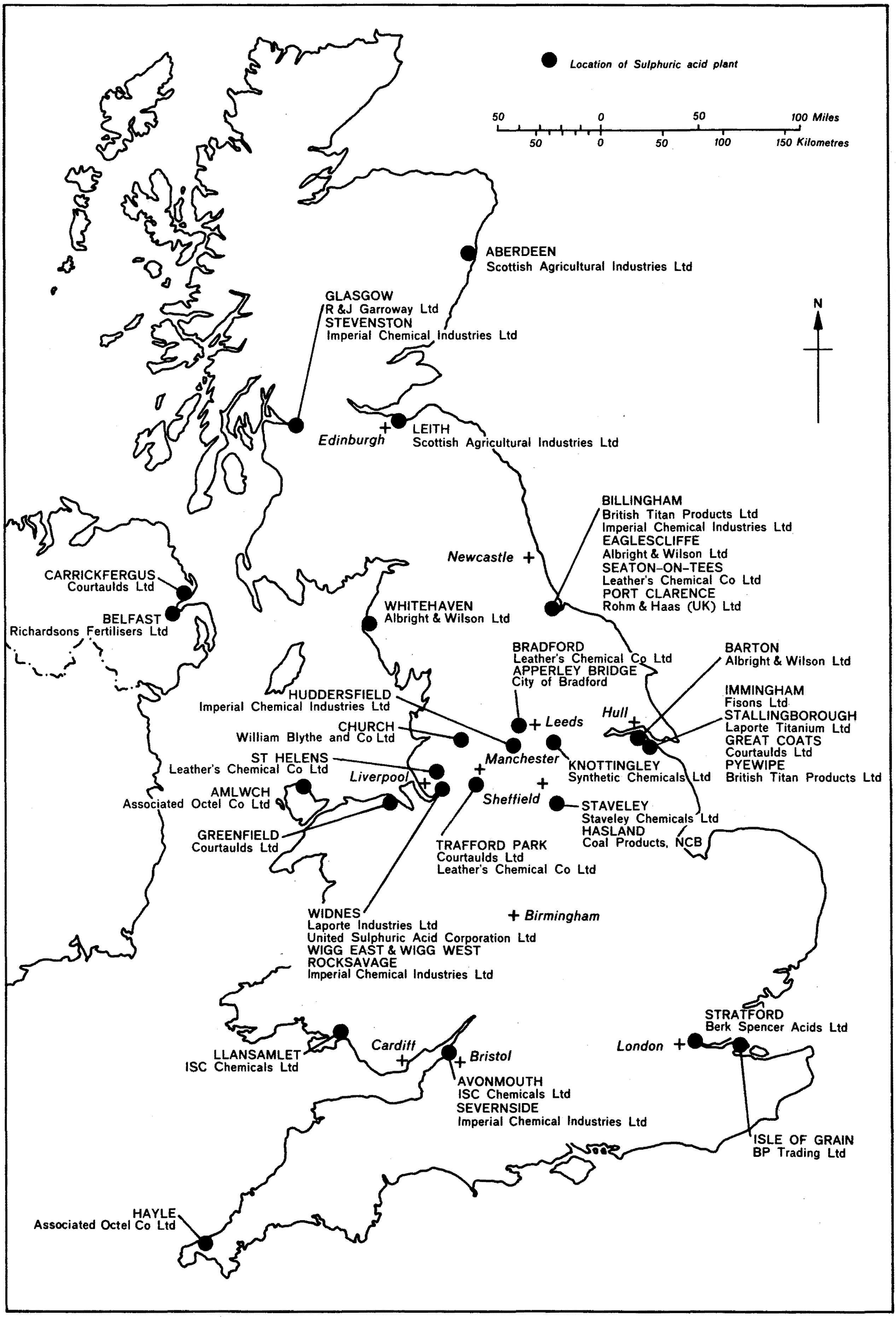

Fig 6 Location of sulphuric acid plants in the United Kingdom, 1972

Hampshire, and from the BP Isle of Grain refinery in Kent. Sulphuric acid production from smelter gas is relatively small in amount in the United Kingdom compared with some other countries. At Avonmouth the smelter acid is used in the production of phosphoric acid by Bristol Chemicals Limited and Imperial Chemical Industries Limited, and also to make hydrofluoric acid. Sulphuric acid is used by the Associated Octel Company Limited in the production of chlorine and bromine. From the remaining domestic sources except anhydrite the acid is produced mainly in small, widely distributed, and generally very old plants.

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