

# Fluorspar

February 2011

## Definition, mineralogy and deposits

### Definition and characteristics

Fluorspar is the commercial name for the mineral fluorite (calcium fluoride,  $\text{CaF}_2$ ), which, when pure, consists of 51.1 per cent calcium and 48.9 per cent fluorine. In nature, however, small amounts of silicon, aluminium and magnesium are also usually present due to impurities and inclusions. Fluorine represents around 0.06 to 0.09 per cent of the earth's crust and predominantly occurs in the mineral fluorspar. It is also found in small amounts in a wide variety of other minerals, such as apatite and phlogopite. Fluorspar generally develops well-formed cubic crystals exhibiting a wide range of colours. Fluorspar has a low melting point, and when added to metallurgical slags, it imparts greater fluidity at lower temperatures, thus making it valuable as a flux in smelting. It is also the principal industrial source of the element fluorine and is most commonly used in the manufacture of hydrofluoric acid. Commercial fluorspar is graded according to quality and specification into acid-grade, metallurgical grade and ceramic grade. Other selected properties of fluorspar are shown in Table 1.

### Mineralogy

Fluorspar rarely occurs as pure  $\text{CaF}_2$  in nature and commonly contains inclusions of gases and fluids, often petroleum and water. The rare earth elements cerium and yttrium can also substitute for calcium. Commercially extracted fluorspar often contains numerous attached and intergrown minerals such as calcite, quartz, barytes, celestite as well as sulphides, such as pyrite and marcasite, and phosphates. Fluorspar can be found in several different crystal forms: it is most well known for well-formed isometric cubic and octahedral crystals but it can also be found as massive and earthy forms (occasionally with columnar crystals), crusts and, rarely, in globular aggregates with a radial fibrous texture. Fluorspar is also

Formula	$\text{CaF}_2$	
Hardness	4	Moh's Scale
Specific Gravity	Normally 3.175-3.184 but can be higher if rich in rare earth elements	$\text{g/cm}^3$
Melting point	1360	$^{\circ}\text{C}$
Boiling point	2500	$^{\circ}\text{C}$
Crystal System	Isometric	
Colour	Various: purple, lilac, golden-yellow, green, colourless, blue, pink, champagne, brown	

Table 1 Selected properties of fluorspar.



Figure 1 Fluorspar from the Northern Pennine Orefield BGS© NERC.

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Deposit type	Brief description	Major examples
Vein deposits	Sheet-like bodies, stockworks and masses of veinlets formed by minerals crystallising from aqueous ('hydrothermal') solutions to fill fissures in rock.	Extensive fluorspar mineralised provinces in the USA, such as the south western province of New Mexico and Colorado. The Bor Undur, Khajuu Ulann, Ayrag and Urgan mines in Mongolia.
Replacement deposits	Carbonate sediments are replaced by fluorspar along joints, faults and contacts with intrusive igneous rocks.	Rio Verde and San Luis districts of Mexico; Cave-in-Rock district of Illinois, USA; Jiangxi province, China; and the Ottoshoop district in South Africa.
Residual concentrations from weathering of primary deposits	Fluorspar from vein and replacement bodies enriched by weathering processes to leave a residual soil profile rich in fluorspar.	Any locality with shallow major vein systems, such as in the Pennine ore field in England; the Lumphun, Petchburi and Ratchaburi Provinces of Thailand; and the Asturias region, northern Spain
Accessory minerals in granitic, carbonatite and alkaline rock complexes	Fluorspar is crystallised from late stage residual melts generally from granitic rocks and is also a common mineral in carbonatite rocks, although it rarely occurs at economic levels.	Crystal Mountain, Montana, USA; Okourusu, Namibia; and Amba Dongar, India.

Table 2 Summary of main fluorspar deposit types.

known for its fluorescence<sup>1</sup>, which is blue or violet, under ultraviolet light. Some varieties are also known for being phosphorescent<sup>2</sup>, thermoluminescent<sup>3</sup> and triboluminescent<sup>4</sup>.

## Deposits

Fluorspar is found in a wide range of geological environments on every continent. Most commonly fluorspar is deposited by hydrothermal<sup>5</sup> solutions sourced from igneous intrusions or deep diagenetic<sup>6</sup> processes. The mineralisation occurs as vein or replacement deposits either by the filling of cavities and fissures or by the replacement of the host rock, typically carbonates. Economic deposits of fluorspar are also found as accessory minerals in igneous rocks, where deposits are associated with pegmatitic granites<sup>7</sup>

or in carbonatite<sup>8</sup> and alkaline rock complexes. Very rarely fluorspar can also be found in lake sediments; for example in Castel Giuliano, Italy, where fluorspar occurs in clay-rich sediments, remobilised from pyroclastic<sup>9</sup> sediments. The key features of the main types of fluorspar deposits are outlined in Table 2.

## Vein deposits

The primary economic source of fluorspar is vein deposits. These are often associated with metallic ores, in particular lead, zinc, silver, and barytes. In vein deposits fluorspar mineralisation is often impersistent and tends to occur as lenticular bodies, separated by barren areas. The most common type of vein deposits are related to fissures, faults and shear zones. These mineralised veins vary in width and length considerably, usually between one to ten metres in width and 60 to 500 metres in length. Some veins may be many kilometres in length e.g. the three-kilometre Muscadroxiu-Genna Tres Montis vein system in Sardinia. Economic deposits can also be found in stockworks and masses of veinlets which occur filling cavities in breccia zones. These often cover large areas but have low CaF<sub>2</sub> contents. For example, the Zwartkloff deposit in

<sup>1</sup> Fluorescence is the absorption and then re-emission of electromagnetic radiation in a different wavelength.

<sup>2</sup> Phosphorescence is the absorption of electromagnetic radiation by a substance followed by re-emission on a slower time scale than fluorescence.

<sup>3</sup> Thermoluminescence is the absorption of electromagnetic radiation by a substance and its re-emission on heating.

<sup>4</sup> Triboluminescence is the generation of light when chemical bonds are broken within a substance.

<sup>5</sup> Hydrothermal refers to geological processes associated with hot fluids.

<sup>6</sup> Diagenesis is the formation of sedimentary rocks from sediment upon burial.

<sup>7</sup> A pegmatite is a coarse grained rock formed by the late stage crystallisation from residual fluids related to granitic magmatism.

<sup>8</sup> A carbonatite is an igneous rock containing more than 50 per cent carbonate minerals.

<sup>9</sup> Pyroclastic refers to explosive igneous rocks.

South Africa is made up of three breccia zones of fluorspar-carbonate veins up to 60 metres wide and 180 metres long extending to depths of 900 metres but the fluorspar grade is only 14 per cent.

Vein type fluorspar deposits occur worldwide. Very large deposits include: the El Hamman vein system in Morocco, which consists of a zone of veins 2.5 kilometres in length with ore widths between 2.5 to 5 metres and grades of 45 per cent fluorite (Fulton and Miller 2006); the Rosiclare-Goodhope vein system in Illinois, USA where the width of the vein could be between 2 and 4 metres thick; and the Osor deposit in Spain, which is now exhausted. Recently exploited deposits in China are vein complexes in terrains of acidic rocks. These include mines in the Zhejiang, Fujian Hebei, Hunan, Guangdong, Anhui, Shandong, Liaoning provinces and Inner Mongolia (Fulton and Miller 2006).

### **Replacement deposits**

In many different geological settings it is possible for metasomatic<sup>10</sup> replacement to alter carbonate rock to fluorspar. Zones of fluorspar replacement are either controlled

by structural breaks, such as joints or faults, which focus replacement along certain, often dolomitised, beds or along contact zones with intrusive igneous rocks. Fluorspar mineralisation is commonly associated with deposits of calcite ( $\text{CaCO}_3$ ), dolomite ( $\text{CaMg}(\text{CO}_3)_2$ ), quartz ( $\text{SiO}_2$ ), galena ( $\text{PbS}$ ), sphalerite ( $(\text{Zn,Fe})\text{S}$ ), pyrite ( $\text{FeS}_2$ ), marcasite ( $\text{FeS}_2$ ), barytes ( $\text{BaSO}_4$ ) and celestite ( $\text{SrSO}_4$ ).

When replacement is confined to distinct beds within carbonate sequences they are often areas of higher porosity<sup>11</sup> than adjacent beds. The flow of mineral enriched fluids from diagenetic processes or igneous activity and mineralisation zones will often be inhibited by impermeable<sup>12</sup> lithologies, such as mudstones. These deposits are found worldwide; with notable examples including the Cave-in-Rock district of Illinois, USA, where deposits can be six metres thick, 150 metres wide and occur over seven kilometres; North Coahuila, Mexico which contains numerous widespread ore bodies; and in the Ottoshoop District of the Transvaal Province, South Africa, where bedded deposits occur in an area 16 kilometres long and 10 kilometres wide within dolomites (Fulton and Miller 2006).

<sup>10</sup> Metasomatic is where rocks undergo a significant chemical change caused by fluid flow.

<sup>11</sup> Porosity is a measure of the amount of voids in a rock mass.

<sup>12</sup> Impermeable means that fluid cannot pass through.



Figure 2 Working vein fluorspar in an open pit from the South Pennine Ore Field, Derbyshire, UK BGS©NERC.

Replacement fluorspar deposits can also be found along the contacts of carbonates and igneous rocks. For example, in the Rio Verde, San Luis Potosi and Aguachile districts of Mexico. The Las Cuevas deposit in the San Luis Potosi region is one of the largest recorded fluorspar ore bodies in the world and has some of the highest grades of fluorspar with about 85 per cent fluorite content (Fulton and Miller 2006). In this deposit fluorspar occurs at the contact between limestones and rhyolites<sup>13</sup>. Metasomatism is related to mineralising fluids flowing along fractures in the contact zone between the country rock and the intrusion.

#### ***Residual concentrations from weathering of primary deposits***

These deposits result from surface weathering of either fluorspar veins or, occasionally, replacement deposits. Surface processes can further concentrate fluorspar, sourced from vein deposits into a clayey and sandy residuum. These deposits can be found anywhere where significant veins crop out at the surface and have undergone weathering. Mining of these weathered deposits is often contemporaneous with working of the vein deposits. Examples of this type of mineralisation are found in the Pennine Orefield of England, the Asturias District of Spain and in Illinois, USA, where deposits are up to 30 metres thick.

#### ***Accessory minerals in granite, carbonatite and alkaline rock complexes***

Fluorspar can become concentrated in residual fluids formed from the crystallisation of igneous rocks and is a common mineral in pegmatites. Generally grades are low and the mineralisation dispersed over large areas. However, they may locally support economic extraction. Fluorspar of this type was worked from the Crystal Mountain deposit in the USA although grades were only sufficient for the production of metallurgical grade fluorspar.

Carbonatite magmas can also concentrate fluorspar to economic grades; for example, in the Okorusu deposit in Namibia fluorspar is sourced from a body of nepheline syenite<sup>14</sup> which has replaced surrounding country rocks of limestone and marble to form large lenticular masses. This type of mineralisation is also seen at Amba Dongar, India, where fluorspar, related to a carbonatite intrusion, has replaced neighbouring country rocks.

<sup>13</sup> Rhyolite is a silica-rich extrusive igneous rock.

<sup>14</sup> Nepheline syenite is an intrusive igneous rock high in alumina.

## **Extraction methods and processing**

### **Mining**



*Figure 3 Fluorspar extraction in the Groverake mine, Northern Pennine Orefield BGS©NERC.*

Fluorspar is mined by both underground and open-pit methods. Open-pit methods are used in areas where veins are exposed at surface or occur at shallow depths of up to 100 metres. At greater depths underground mining methods are used. Underground mining involves chiefly two methods: shrinkage stopeing or sub-level stopeing where broken ore supports the stope<sup>15</sup> walls; and room and pillar mining where 'pillars' of rock are left in place to support the excavation.

Vein deposits, when near vertical, are generally mined by shrinkage stopeing where ore is accessed from below, or sub-level stopeing where veins are accessed from horizontal shafts, thus eliminating the need to work underneath potentially unstable ground. Ore is blasted and falls to the bottom of the stope to be extracted. The average mining depth of vein deposits is typically between 200 and 300 metres but the actual depth depends on the size and grade. The typical grade of these deposits varies between 30 per cent and 70 per cent CaF<sub>2</sub> with occasional higher-grade orebodies.

For flat-lying stratiform deposits, such as those in Illinois, USA, the room and pillar (also called pillar and stall) mining method is used generally at shallow depths, where

<sup>15</sup> A stope is an excavation used to extract ore.

surface disturbance needs to be kept at a minimum. The width of the rooms and pillars is dependent on ground conditions. Pillars are left in place in a regular pattern while the rooms are mined out. Room and pillar methods are well adapted to mechanisation.

In areas where orebody width, depth of overburden and strength of the wallrocks permit, open-pit mining methods are employed. The rock that lies above the orebody (the 'overburden') is excavated and stored nearby and the exposed ore is extracted. Both capital and working costs are far less for open-pit operations than for underground mines. At the end of mining the pit is normally back-filled using the overburden and the area is restored to other uses. In areas where mineralised veins are weathered from surface to depths of up to 70 metres, the ore may be mined using draglines, scrapers or power shovels, such as in the Southern Pennine Ore Field in the UK.

### Processing

Fluorspar ores are commonly blended prior to use in order to maintain a constant feed grade to the beneficiation<sup>16</sup> plant. The ore is generally crushed, washed and screened before processing (Figure 4), although in some

cases very high-grade fluorspar can be shipped directly after the screening process. Most modern beneficiation plants use a combination of gravity and froth flotation processes. Gravity concentration using liquids separates out the gangue<sup>17</sup> minerals to produce either a coarse metallurgical grade fluorspar or to provide feed for a flotation plant producing acid or ceramic grade fluorspar. Prior to flotation, the ore is ground very finely to liberate impurities and then fed into tanks containing an agitated chemical solution.

The grains of fluorspar preferentially stick to bubbles rising through the tank and overflow the tank rims as froth. In some cases, one or more concentrates of lower grade may be produced in addition to the higher grade. Such lower grade concentrates are sold as ceramic grade, or are pelletised and sold as metallurgical grade fluorspar. Due to the increasing demand for acid grade fluorspar Mexican fluorspar producer Mexichem is developing technology to enable the hydrofluoric acid production from fluorspar with high arsenic contents (a common impurity). This could significantly increase the number of mineral deposits from which acid grade fluorspar can be produced.

<sup>16</sup> Beneficiation is the upgrading of ore to commercially accepted grades.

<sup>17</sup> Gangue are waste products from ore processing.

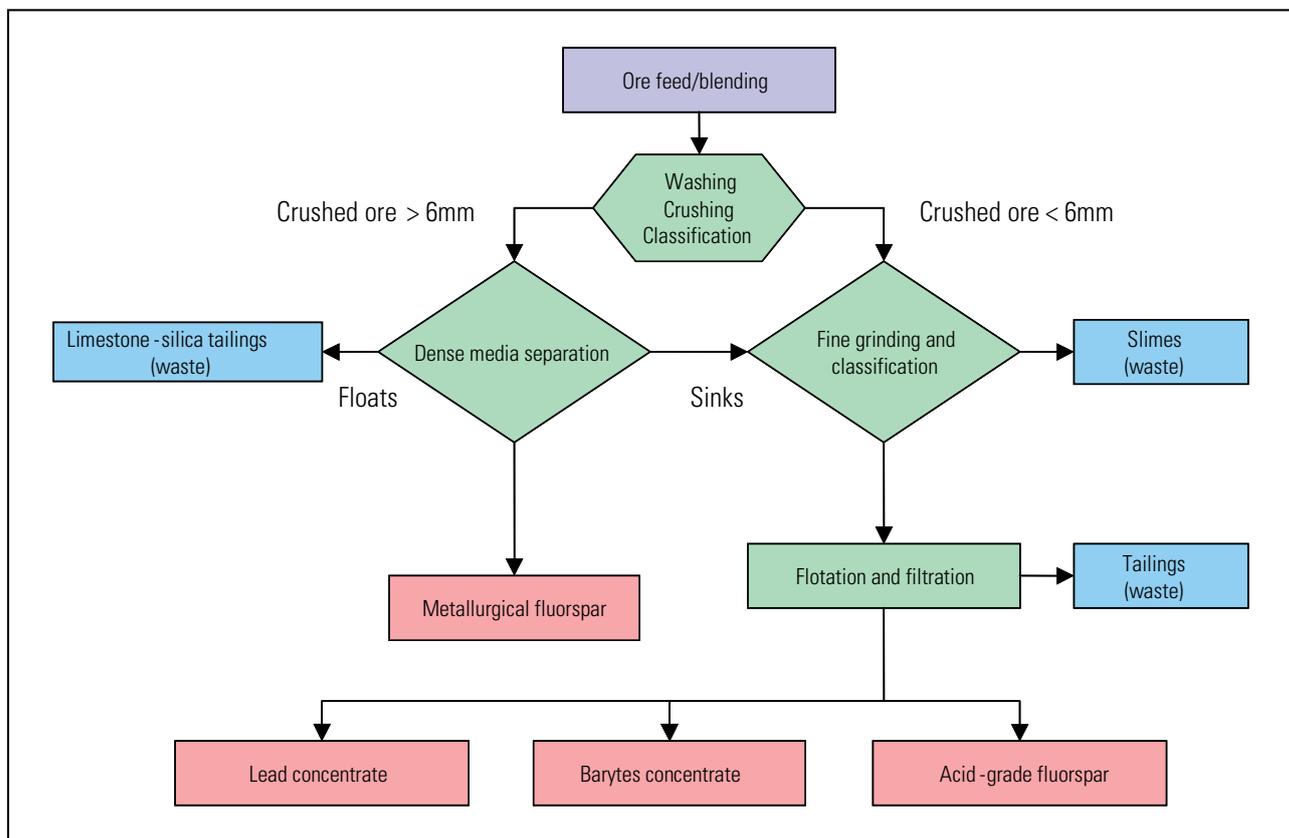


Figure 4 Simplified process sheet for fluorspar and by-production (based on UK production).

## Specification and uses

### Specification

Commercial fluorspar is graded according to quality and specification. These grades are based on fluorspar content ( $\text{CaF}_2$ ) and the amount of impurities (such as calcite,  $\text{CaCO}_3$ , quartz,  $\text{SiO}_2$ , sulphur, S, arsenic, As, and lead, Pb). The grades are as follows:

- acid grade or 'acidspar' (minimum 97%  $\text{CaF}_2$ , up to 1.5%  $\text{CaCO}_3$ , 1.0%  $\text{SiO}_2$ , 0.03–0.1% S, 10–12 ppm As, 100–550 ppm Pb);
- metallurgical grade or 'metspar' (minimum 80%  $\text{CaF}_2$ ; maximum 15%  $\text{SiO}_2$ , 0.3% S, 0.5% Pb);
- ceramic grade (80–96%  $\text{CaF}_2$ , up to 3%  $\text{SiO}_2$ ).

### Uses

The grade of fluorspar determines its end-use. Nearly two thirds of the world's production is for the manufacture of hydrofluoric acid, a feedstock for many different chemical processes. Approximately one third of fluorspar produced worldwide is of metallurgical grade and is used primarily as a flux in steelmaking and in the production of aluminium. A small proportion of fluorspar produced is ceramic grade which is used in the production of opaque glass and enamels (Figure 5).

### Hydrofluoric acid

Acid grade fluorspar is used predominantly in the production of hydrofluoric acid (hydrogen fluoride, HF). HF is the

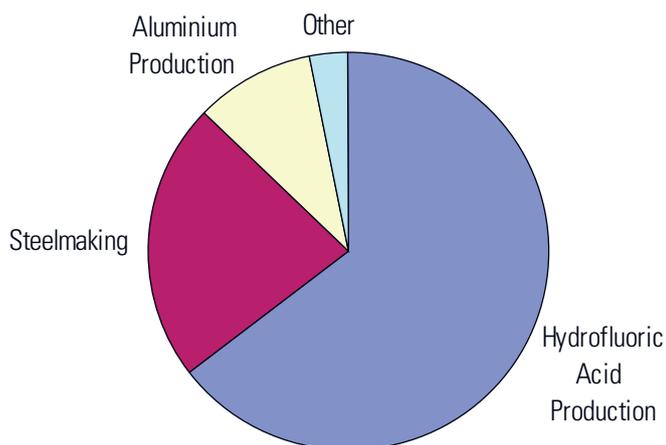


Figure 5 Common fluorspar end-uses (proportions are indicative).

basis for all fluorine-bearing compounds, which include important pharmaceuticals and agrochemicals. Production is mostly in China, the US, Japan and Europe.

HF is produced by heating a mixture of acid-grade fluorspar and concentrated sulphuric acid (Figure 6) and is a key intermediate in the production of a wide range of organic and inorganic fluorine-bearing chemicals. Deleterious impurities in acid grade fluorspar are silica, carbonates and sulphides. Silica is particularly undesirable as it causes losses in the yield of HF and its content should be less than one per cent. Calcium carbonate increases the usage of sulphuric acid and should be less than 1.5 per

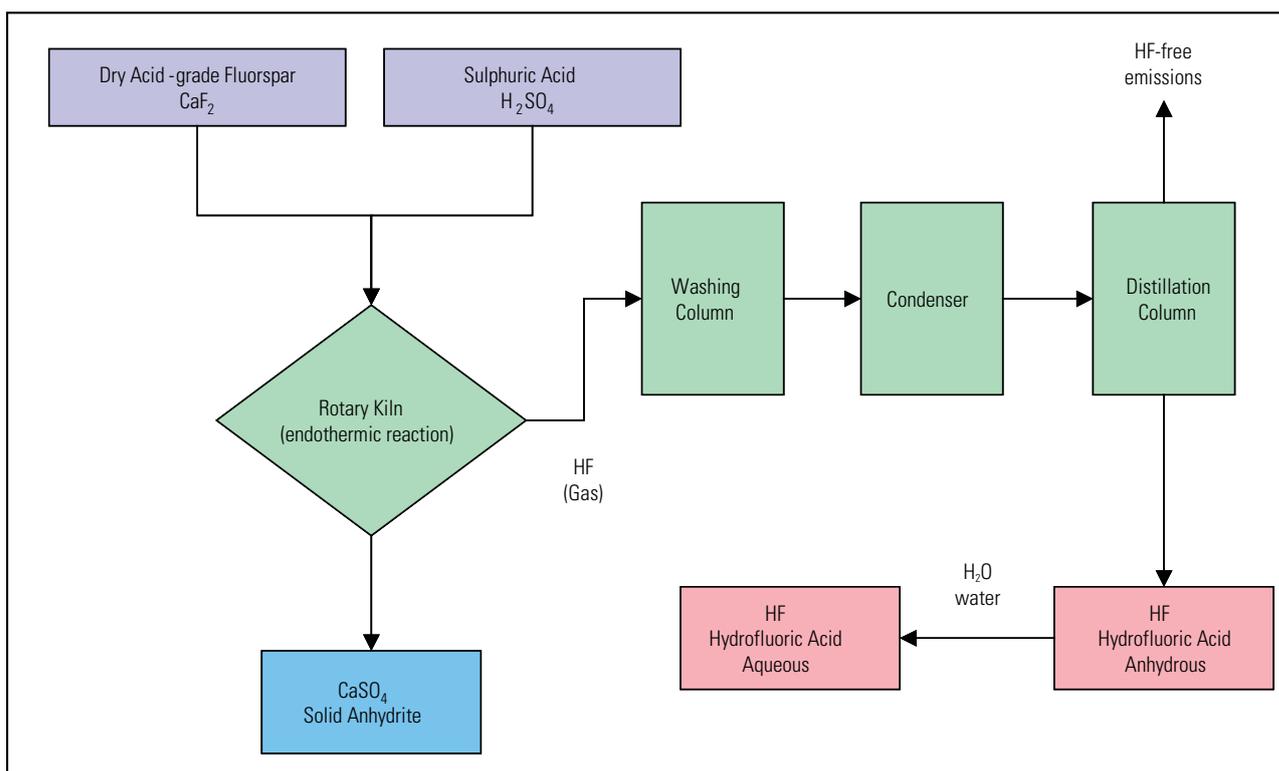


Figure 6 Simplified flowsheet for the production of hydrofluoric acid (HF) from dry acid-grade fluorspar.

cent. There are also stringent limits on sulphur, arsenic and phosphorus contents. Typically 2.2 tonnes of fluorspar are required per tonne of HF produced.

Approximately 60 per cent of global HF production is used in the production of a wide range of fluorochemicals, which are used as refrigerants, non-stick coatings, medical propellants and anaesthetics. Small amounts of hydrofluoric acid are also used as a catalyst in petroleum alkylation<sup>18</sup>, for stainless steel pickling<sup>19</sup>, for metal etching in electronics manufacture, and in uranium processing.

### **Fluorocarbon chemicals**

Historically, the largest group of chemicals that requires HF in their manufacture are chlorofluorocarbons (CFCs). CFCs were first used in the 1930s by manufacturers seeking more benign chemicals than ammonia and sulphur dioxide in refrigeration units. Other uses were quickly established, such as:

- Aerosol can propellants
- Blowing agent for foam (where fluorine compounds are used as an agent to produce a range of plastics such as polyurethane and polystyrene)
- Fire extinguishers
- Refrigerant agents (fluorine compounds can be used for heat transfer processes in numerous applications including air conditioning, transport, commercial and domestic refrigeration and food processing)
- Strongly evaporating cleaning agents.

In 1974, chlorine released from CFCs was demonstrated to be a cause of ozone depletion in the stratosphere. Consequently the Montreal Protocol was created in 1987 and has been ratified by 196 nations. This Protocol called for an immediate reduction in the production and use of non-essential CFCs, the majority of which are in refrigeration applications. In addition, both the EU and USA have passed legislation limiting the use of CFCs, (such as the USA's 1990 Clean Air Act). Intentional venting of CFC gases during the maintenance and decommissioning of appliances, and industrial process refrigeration have also been outlawed.

Hydrogen-containing chlorofluorocarbons (HCFCs), which contain a larger proportion of fluorine per unit weight, were introduced as transitory replacements for CFCs. However, these too are due to be phased out. EU regulation banned production and import of virgin HCFCs at the

<sup>18</sup> Alkylation is a process used in the upgrading of petroleum products.

<sup>19</sup> Pickling is the surface treatment of metals to remove impurities.



*Figure 7 Mexichem's hydrofluoric acid plant at Runcorn ©Mexichem.*

end of 2010 and by 2015 all HCFC chemicals, including recycled ones, will be banned.

HCFCs are being replaced by hydrofluorocarbons (HFCs) which contain no chlorine, and even more fluorine, although they are more expensive. Whilst HFCs have no ozone-depleting potential they are listed as a 'greenhouse gases'. Consequently, the use of HFCs is restricted by the Kyoto Protocol on greenhouse gases. As a result applications of HFCs have to be designed to minimise leakage and ensure efficient recycling. Future demand for HF, and thus acid-grade fluorspar, now that CFCs are no longer produced and HCFCs are being phased out, may depend on the success of alternatives, such as HFCs with lower greenhouse gas potential, and the emergence of novel fluorine-based chemicals that can be successfully marketed on a large scale.

### **Metallurgical use**

Metallurgical grade fluorspar is used as a flux in open-hearth oxygen and electric arc furnaces where it acts to reduce slag viscosity, lowers the melting point and removes impurities such as sulphur and phosphorus from steel. Metallurgical grade fluorspar is also used in the production of aluminium, as aluminium fluoride (AlF<sub>3</sub>) is a component of the molten bath in the electrolytic reduc-

tion of alumina to aluminium metal. Higher grades of fluorspar are also used in the manufacture of stainless steel.

### Other uses

Ceramic grade fluorspar is used in the glass and ceramic industries where it is needed to produce opal glass and opaque enamels; smaller quantities are used in the manufacture of magnesium and calcium metal and welding rod coatings. Fluorspar can also impart low dispersions to camera and telescope lenses and is used in the manufacture of high quality optics.

New uses for fluorine in the form of fluoropolymers in the plastics and electronic industries have emerged in the past decade which could replace demand lost due to declining CFC production. Fluoropolymers (e.g. the well known PTFE resin or Teflon®) are remarkable for their thermal stability, high chemical inertness, strong electrical insulation and very low coefficient of friction. As a result there is a myriad of products and applications for which markets are continually being developed. For example, Teflon is used to create a non-stick coating on frying pans, polyvinylidene fluoride or Kynar can be used for high specification paints due to its high resistance and color retention, Ethylene tetrafluoroethylene, or Fluon, is used in architecture to replace glass, where it is stronger, cheaper and transmits more light.

A second rapidly growing market is nitrogen trifluoride (NF<sub>3</sub>), which is widely used as an inert cleaning gas in the manufacture of semi-conductors and LCD screens.

Inorganic fluoride compounds (usually barium fluoride) are also important in ceramic applications where they aid ceramic production by acting as a flux and give the final product its opaque properties.

Fluorspar is also used in a wide range of chemicals vital for the manufacture of electrical components in the form of silicon-based semi-conductors, catalysts in petrochemical production, pharmaceuticals, herbicides, pesticides, crystal glass manufacture and the processing of uranium for nuclear fuel.

## World resources and reserves

World resources<sup>20</sup> of fluorspar are estimated at 500 million tonnes. Fluorspar resources are widespread globally and

<sup>20</sup> A mineral resource is a concentration of minerals or a body of rock that is, or may become, of potential economic interest for the extraction of a mineral commodity.

major deposits can be found on every continent. World reserves<sup>21</sup> of 100 per cent equivalent CaF<sub>2</sub> are estimated at 230 million tonnes (equating to ore reserves of 374 million tonnes). South Africa has the world's largest fluorspar reserves, which occur mostly in vast low grade deposits often with high production costs. Mexico and China also have major reserves and host significant fluorochemicals industries (Table 3).

	Million tonnes contained fluorspar	Percentage of total world reserves
South Africa	41	17.8
Mexico	32	13.9
China	24	10.4
Mongolia	12	5.2
Spain	6	2.6
Namibia	3	1.3
Kenya	2	0.9
Other Countries	110	47.8

Table 3 World identified reserves of fluorspar, 2010. Source: Miller 2011.

## World production

World production of fluorspar increased rapidly between 1950 and the early 1970s when it levelled off (Figure 8). The apparent increase in fluorspar production between 1950 and 1975 can, in part, be attributed to improved reporting by several countries that are significant producers. Other reasons for historically increasing production of fluorspar can be closely tied in with the manufacture of steel, aluminium and chlorofluorocarbons (CFCs).

Prior to 1980, steel manufacture requirements accounted for 30–50 per cent of global fluorspar consumption, but this has declined to around 20 per cent due to the expansion of the fluorochemicals industry and more efficient steel production. Technology is also changing in the aluminium industry such that fluorine derived from fluorspar is being replaced by fluorosilicic acid. Historically

<sup>21</sup> A mineral reserve is the part of the resource which has been fully geologically evaluated and is commercially and legally mineable with current technology.

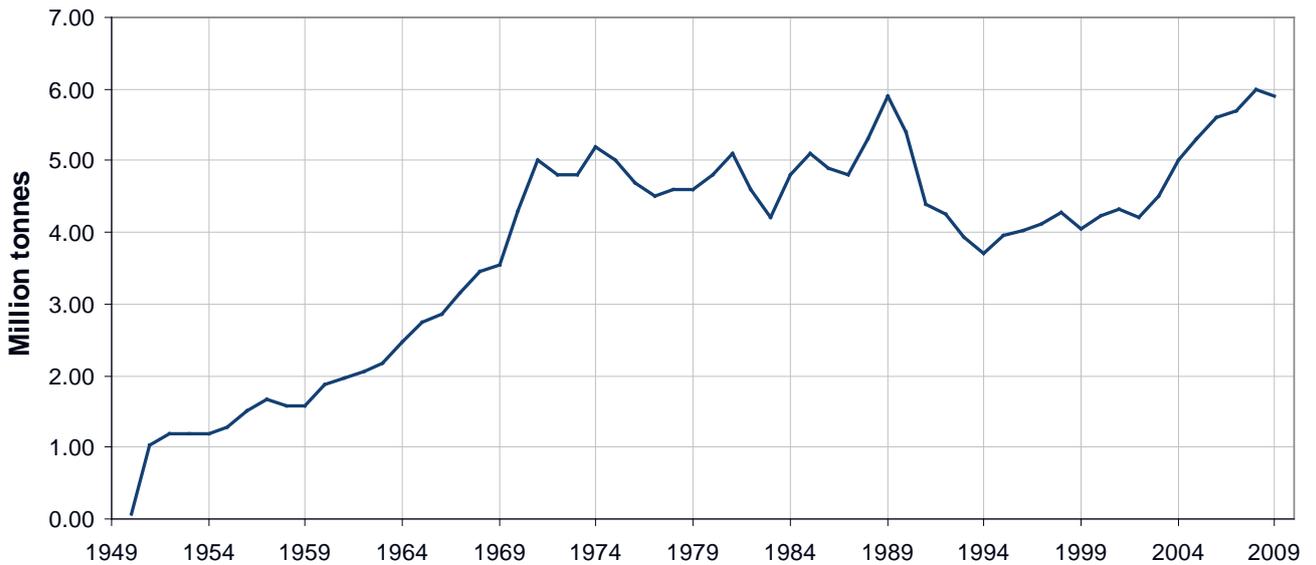


Figure 8 World production of fluorspar, 1950–2009. Source: World Mineral Statistics, British Geological Survey.

the aluminium manufacturing process has consumed significant amounts of fluorine due to losses in the aluminium production process. However due to modern manufacturing processes and better practice these losses have been significantly reduced. Consequently fluorspar demand for this application has fallen.

In the chemical sector, the global ban on CFC propellants caused a significant reduction in production from 1989 onwards. This is reflected in the significant drop in fluorspar production shown in Figure 8. However, as CFC manufacture as a refrigerant and aerosol component was phased out, fluorine-based replacements (HFCs), which actually use more fluorspar, began to offset the reduced demand from lower CFC production. Consequently the net decrease in world production from 1989–1994, caused by the fluorochemicals industry adjusting to the CFC ban, was followed by slow growth in the fluorspar market from 1994–2003.

In the past twenty years production has declined in all the countries of the industrialised ‘western’ world but has increased dramatically in China and some other developing countries, such as Mongolia (Figure 9). Overall this has led to a rise in world production over the last 10 years to record levels in 2008. The rapid growth of Chinese fluorspar production, rising from a 10 per cent share of global production in 1980 to 55 per cent in 2009, is notable. In 2009 (Figure 9) 81 per cent of the world’s fluorspar was produced by only three countries, with China clearly dominant.

This rise in China’s output is mirrored by falls in production in Europe and, to a lesser extent, Africa and Russia.

European output has fallen from almost a quarter of world production in 1980 to 12 per cent in 1992 and just three per cent in 2009. There is also no domestic production of fluorspar in the USA in 2009, which had a two per cent market share in 1980.

Global consumption is dominated by China, where demand is currently matched by domestic production. The USA, which consumes around a tenth of world production, and Europe, which consumes around a quarter of global fluorspar production, are heavily reliant on imports of fluorspar. Almost the entire fluorine requirements of the USA are met by fluorspar imported from Mexico and China and recovered from fluorosilicic acid during phosphate fertiliser production.

World production of fluorspar decreased by three per cent in 2009 compared to 2008. This is the first decrease in annual production since 2003 and was caused by a decrease in demand due to the global financial crisis; this especially affected the demand for metallurgical grade fluorspar due to weakened demand for steel and aluminum from the construction and automobile sectors (Clarke 2009a). The decrease was less than predicted due to sustained demand for fluorspar by the fluorochemicals industry (Roberts 2009).

China produced 55 per cent of total world production in 2009 although output was 1.5 per cent lower than in 2008. Over the five years of 2005–2009 China’s output has increased by 18.5 per cent. The world’s second largest producer, Mexico, showed a small production decrease in 2009 compared to 2008, although production rose by

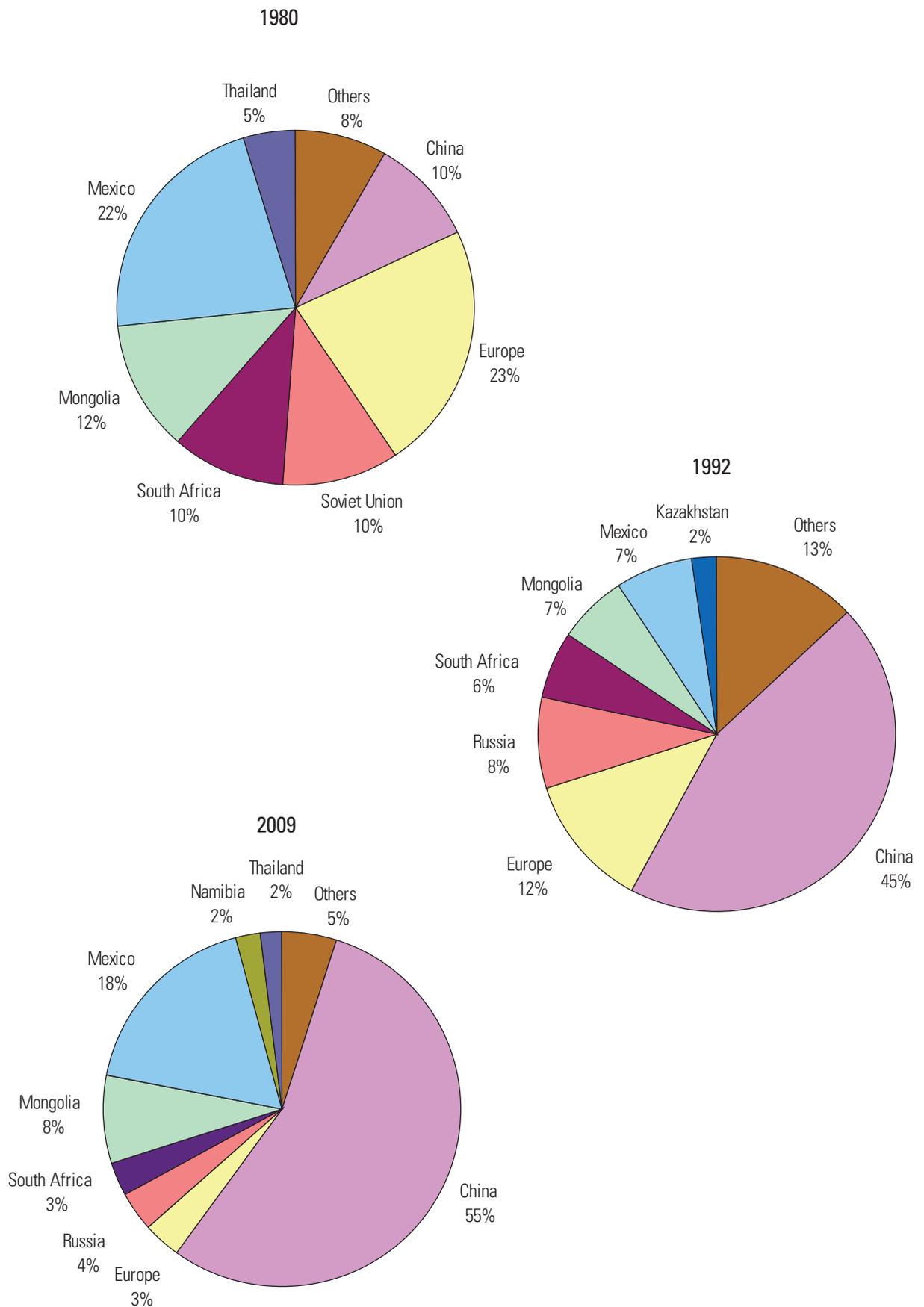


Figure 9 World fluorspar production, in 1980, 1992 and 2009. Source: World Mineral Statistics database, British Geological Survey.

19.5 per cent between 2005 and 2009. Mongolia, the world's third largest producer, increased its production in 2009 by 37 per cent. In part, this was due to the completion of an extensive modernisation project at the Bor-Undur mineral processing plant.

European production decreased in 2009 compared to 2008 with the largest producers, Russia and Spain, decreasing output by 22 and 18 per cent respectively. Europe's only other producers, since production finished in France and Italy in 2006, are Germany and the United Kingdom. In Germany production increased by three per cent in 2009 compared to 2008 but in the UK production fell by almost 50 per cent and ceased entirely at the end of 2010.

## World trade

The main fluorspar-exporting countries in 2009 were Mexico, Mongolia, China and South Africa (Figure 10), which together accounted for 86 per cent of all fluorspar exports.

China and Mongolia export to most of the fluorspar-importing countries. Together they meet the entire import requirements of Japan and around 47 per cent of the USA's annual fluorspar imports (Miller 2011). China is steadily decreasing its exports of raw fluorspar. It is now concentrating on the development of a fluorochemicals industry and is increasing exports of higher value fluorspar-derived

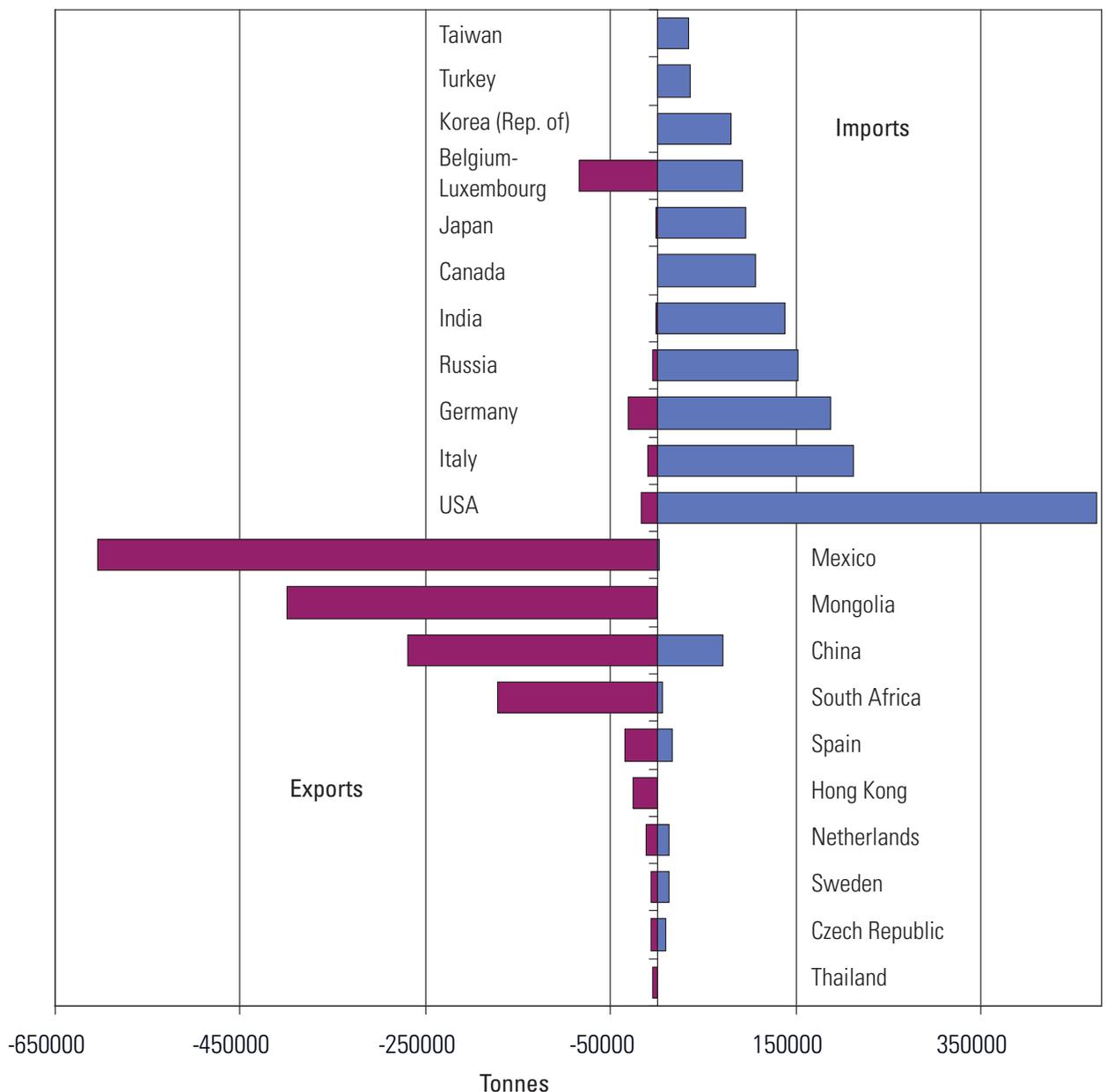


Figure 10 Major fluorspar importing and exporting countries, 2009. Source: World Mineral Statistics Database, British Geological Survey 2010a and UN comtrade database.

products (Roberts 2010). This decrease in exports from China is due to a number of trade restrictions, such as export quotas, duties, extra licensing and price requirements; this has led to a WTO (World Trade Organisation) investigation against China into unfair practices (Industrial Minerals 2010a). A large proportion of exports from Mexico goes directly to the USA, with the remainder being exported to Europe. African producers mostly export to countries of the European Union (EU).

There are no net exporters of fluorspar in Europe and all EU member countries are reliant on imports. Domestic UK production from Glebe Mines was not sufficient to meet the chemical industry's demand for fluorspar, making the UK a net importer in 2009 with imports of about six million tonnes.

## Prices

The price of fluorspar has seen greater fluctuations than most industrial minerals over the past 20 years and is closely associated with market demand for hydrofluoric acid, chemicals, aluminium and steel. The general trend in prices since 2008, based on quarterly averages, is shown in Figure 11. The majority of fluorspar is traded on annual contracts and only small amounts are sold on the open market.

Up to 1997 metallurgical grade fluorspar had always been around half the price of acid grade, which is to be expected considering their quite different fluorine contents. After 1997 there was a sudden convergence in price as a direct consequence of China exporting large tonnages of

acid grade fluorspar without commensurate quantities of metallurgical grade.

After remaining relatively constant for many years fluorspar prices rose rapidly between 2007 and 2009. This was principally due to a tightening of supply as a result of increased consumption within China and the implementation of restrictive Chinese export quotas. There have also been significant increases in freight costs in recent years.

In mid 2009 there was a rapid decrease in prices from the unprecedented price peaks of 2008 and early 2009 due to weakened demand from the fluorochemical sector. However prices still remained higher than those of 2007. This was probably due to continuing demand, mainly from the emerging economies, and decreasing supply from China. During 2010, fluorspar prices in all grades remained nearly constant.

## Recycling and substitution

As fluorspar is consumed in the production of HF and in subsequent chemical manufacturing processes, recycling of the mineral is impossible. There are several alternatives sources of HF, including calcium fluoride, depleted uranium hexafluoride, sodium fluoride and sodium fluorosilicate. However the use of fluorosilicic acid is the only one which could have a significant impact on global fluorspar extraction (Clarke 2009b).

Fluorosilicic acid (FSA) is produced in large quantities as a by-product during the production of phosphoric acid for fertiliser manufacture. It is used as a source of fluorine in

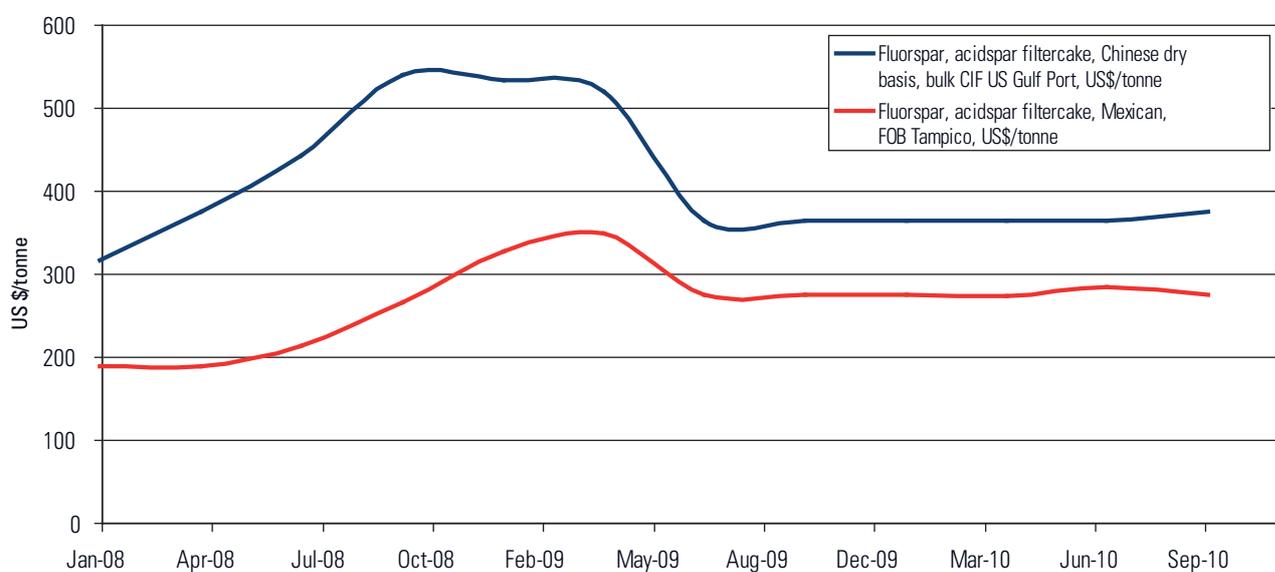


Figure 11 General trend in the price of fluorspar (US\$ per metric tonne) from 2008 to 2010 based on quarterly averages. Source: Industrial Minerals 2010. [www.indmin.com](http://www.indmin.com).

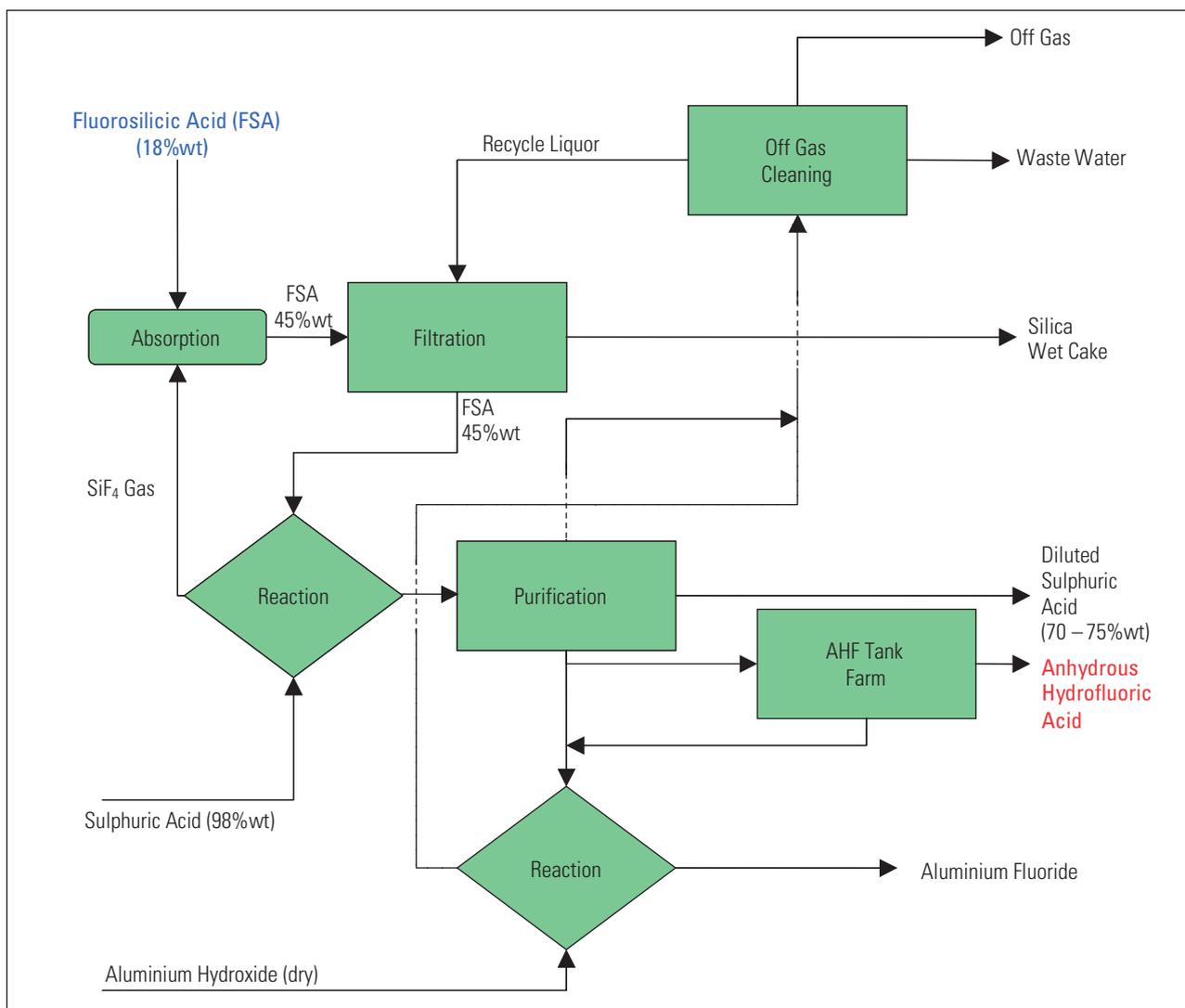


Figure 12 Simplified flowsheet for the production of HF from fluorosilicic acid.

some parts of the world. At present, the UK has no phosphoric acid production. FSA is widely used in the manufacture of aluminium fluoride, and also for the fluoridation of drinking water — the USA produced 55 000 tonnes of 92 per cent fluorspar equivalent by this method in 2009. HF is produced from FSA by the decomposition of aqueous FSA in the presence of sulphuric acid, with the products being  $\text{SiF}_4$  and HF (Figure 12) (Dreveton 2000). Until recently, the FSA route to produce HF was more expensive than the fluorspar route, but this situation is changing as new technologies make production of HF from FSA cheaper (Clarke 2009b).

There is currently a major drive to replace fluorine-based compounds used in many applications with more environmentally friendly alternatives. Much research is being undertaken by the fluorochemicals industry into low greenhouse potential HFCs, especially for air-conditioning

applications. However, many new compounds developed so far have proved to be highly flammable and do not meet safety requirements. The technology to replace many existing HFC chemicals with others which have lower greenhouse gas potential is predicted to come on stream in the next 5–10 years (Roberts 2010).

There is potential to replace fluorine-based chemicals with hydrocarbon-based refrigerants (butane, propane). Many leading manufacturers, such as The Electrolux Group, have committed to using hydrocarbon-based refrigerants. Although the take up of hydrocarbon refrigerants has been very slow (they are more flammable and less efficient), it is possible that this market for fluorine will decline. For foam blowing applications it is also possible to use hydrocarbons as a replacement for HFCs.  $\text{CO}_2$  and  $\text{H}_2\text{O}$  substitutes for fluorochemical foam blowing agents are also under development.

## Focus on Britain

### Resources

In the United Kingdom fluorspar-barytes-lead mineralisation occurs mainly in two areas, the Southern Pennine Orefield and the Northern Pennine Orefield (Figure 13). The mineral occurs in limestones in steeply inclined east–west and east-north-east to west-south-west fissure veins (locally known as rakes) with individual veins up to several kilometres in length and up to 10 metres wide. Groups of thin veins may be developed locally.

In the Southern Pennine Orefield the main mineralisation is confined to the eastern part of the district, below the highest limestones that lie beneath a mudstone cover. Genetically, the mudstone is thought to have acted as an impermeable cap-rock to the mineralising fluids. Volcanic rocks interbedded with the limestone are generally barren, but occasionally allow the development of sub-horizontal deposits or ‘flats.’ There is a broad, cross-country, mineral zonation of fluorspar-barytes-lead veins, with fluorspar being the dominant mineral in the east, and barytes and calcite becoming progressively more abundant westward. However, the zones are poorly defined and there is considerable overlap.

Most fluorspar deposits in the Northern Pennine Orefield are found in near-vertical veins within thin alternating Carboniferous limestones, sandstones and shales and occasionally in basic intrusives associated with the Whin Sill. Sub-horizontal sheets of replacement fluorspar mineralization locally occur in favourable lithological horizons adjacent to some of the larger veins. Along the southern margin of the orefield fluorspar deposits occur in massive Carboniferous limestone.

Following a long history of extraction many of the major veins have been depleted as sources of open-pit fluorspar. Exploration has been directed towards finding concealed orebodies related to cavity infillings and replacement deposits in receptive limestone. The mineralogy of these deposits does not correspond with the broad mineral zones seen in the veins. Consequently fluorspar and barytes resources may occur more extensively in a westerly direction than was previously thought.

### Reserves

Current permitted reserves of fluorspar available to the sole operator, Glebe Mines, before its closure in December 2010 (Industrial Minerals 2010c) principally reside in a small number of planning permissions for open-pit and underground extraction. All of these are located in

the Southern Pennine Orefield, within the Peak District National Park. The natural variability of fluorspar mineralisation, the unpredictability resulting from a long history of surface and underground working, together with variations in the cost of extraction, processing and the global price of fluorspar, makes it difficult to define accurate reserve figures. The reserve estimates given below were made in October 2009.

A total of 1 215 000 tonnes of ore are accessible by open-pit working at Tearsall, Peak Pasture and High Rake. Consent for extraction at Tearsall was granted in 2009 for a duration of 6 years. High Rake is close to exhaustion and consent for extraction came to an end in 2010. There is currently no working at Peak Pasture.

About three million tonnes of fluorspar ore are accessible from underground mines at Milldam and Watersaw West. Neither mine is currently operating. Before its closure Glebe Mines was working toward re-opening Milldam Mine where the bulk of these reserves is located and which is permitted until the end of 2013. Watersaw has planning consent for extraction until 2015.

### Structure of the industry

Glebe Mines Ltd, until recently, was the only significant producer of fluorspar in the UK and is owned by the UK-based chemical manufacturer INEOS. In February 2010, INEOS announced the sale of its fluorine chemical plant at Runcorn in Cheshire to the Mexican-owned chemical producer Mexichem. Glebe Mines remained under INEOS ownership. In December 2010 Glebe announced it would cease mining and processing by the end of 2010 due to a failure to secure future funding for the plant, thus ending fluorspar production in the UK.

Glebe Mines operated the Cavendish Mill, near Stony Middleton in the Peak District National Park. Fluorspar ore to supply the mill was mainly derived from Glebe’s own operations, but smaller ‘tributer’ producers also supplied some ore. The Cavendish Mill was the only source of fluorspar in the UK. Glebe Mines also produced by-product barytes, lead concentrate and limestone aggregates.

The sole consumer of acid-grade fluorspar from this operation was the HF and fluorochemicals manufacturing facility, now operated by Mexichem in Runcorn (Figure 13). This site produces a range of fluorochemicals including HFC 134a, which is a replacement for CFCs and HCFCs, and was formerly reliant almost entirely on fluorspar produced in England.

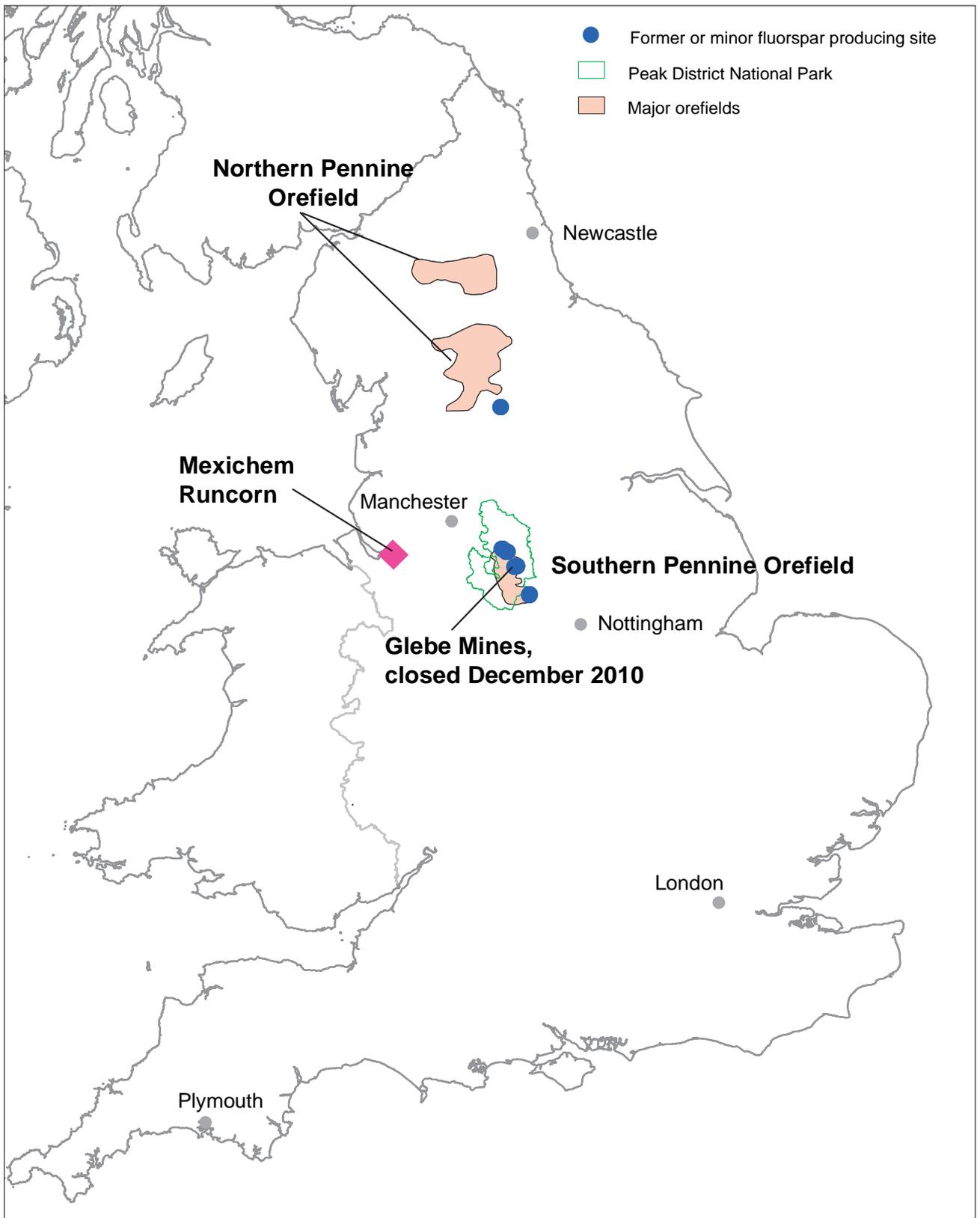


Figure 13 The distribution of former fluorspar mining areas in Great Britain, the location of the Mexichem HF facility is also shown. Source: British Geological Survey 2010c. OS topography © Crown Copyright. All rights reserved. BGS 100017897/2011.



Figure 14 Flourspar processing at the Cavendish Mill BGS©NERC.

Over the last 30 years there have been a number of other ventures to establish flourspar mining and processing operations both in the Southern and Northern Pennine Orefields, none of which have proved economically sustainable.

The Milldam Mine at Great Hucklow was formerly an important source of flourspar. However, easily accessible ore has been exhausted and some of the remaining mineralisation consists of a fine intergrowth of flourspar and silica

at sub-microscopic levels, making it difficult to process the ore to provide a saleable product. The mine is currently on care-and-maintenance basis.

### Production

From 1874 to 2009 a total of 8.86 million tonnes of flourspar was produced in the UK. Flourspar production expanded considerably during the late 1960s and early 1970s due to increasing demand from the chemical and steel industries. Peak output of 235 000 tonnes was achieved in 1975. However, production declined from the early 1980s (Figure 15).

The Southern Pennine Orefield typically accounted for over 75 per cent of historical production and almost all production since 1999. A major expansion in flourspar mining and processing capacity took place in the Northern Pennines in the late 1970s, but this proved unsustainable in the face of declining home and export markets, and low cost imports. Following a period of rationalisation, a long history of flourspar and lead mining in the Northern Pennine Orefield came to an end in 1999 with the closure of the Frazer's Hush and Groverake mines near Rookhope, Durham. A resumption of mining is unlikely in the foreseeable future.

With the closure of Glebe Mines in December 2010 the UK no longer produces flourspar, except for minor production for mineral specimens.

### Consumption

Acid-grade flourspar is believed to account for almost all of the flourspar consumed in the UK, with a minor amount of imported metallurgical grade used in steelmaking. Annual UK consumption of flourspar in 2009 (domestic production plus net imports) is estimated to be approximately 43 000 tonnes. Acid-grade flourspar is believed to account for

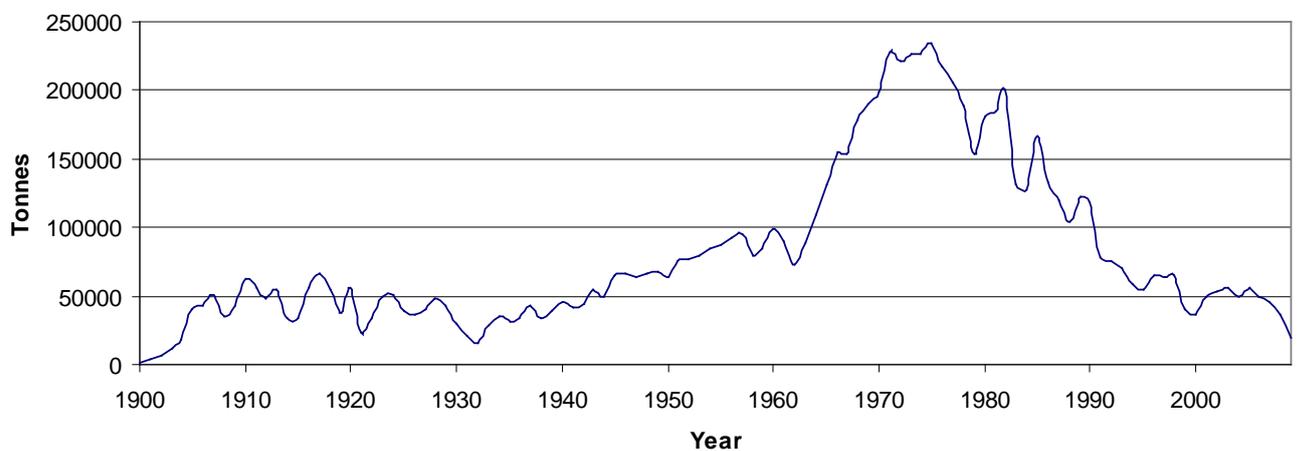


Figure 15 Sales of flourspar in England, 1900–2009. Source: World Mineral Statistics database, and Mineral Dossier: flourspar, British Geological Survey

over 90 per cent of the total (Table 4), of which nearly all is used in the manufacture of HF.

Domestic sales	37 000 tonnes
Net imports	6 133 tonnes
UK Consumption (estimated)	43 133 tonnes

Table 4 UK consumption and sources of fluorspar, 2009. Source UK Minerals yearbook 2009, BGS 2010.

The main consumer of fluorspar in the UK, is Mexichem (formerly Ineos Fluor Ltd) in Runcorn, Cheshire (Figure 13). Until 2004 fluorspar was also used by Rhodia Organique Fine Ltd, which operated an anhydrous HF plant at Avonmouth.

### Trade

Prior to the mid-1980s the UK was a net exporter of fluorspar but subsequently became a net importer as indigenous supplies became less competitive. UK imports of both acid and metallurgical grade fluorspar are now chiefly from Mexico and China.

### By-products of UK fluorspar production

Lead and barytes were important by-products of fluorspar extraction in the South Pennine Orefield. Fluorspar processing at the Cavendish Mill produced high-purity acid-grade fluorspar, together with barytes and lead concentrates. By weight around 15–20 per cent of total output at Glebe Mines was barytes and up to one per cent was lead (excluding aggregates). The lead concentrate was one of only two sources of lead produced in the UK (the other being from gold mining in Northern Ireland), and was traded locally. The barytes produced at the Cavendish Mill plant was sold to Viaton Industries (where it was further processed for specialised uses) and into the drilling fluids market. This was the second-most important source of barytes in the UK and the only source in England.

Limestone was also produced during the fluorspar beneficiation process (Figure 4). This material was sold for aggregate use but was not subject to the Aggregates Levy (a tax on all primary aggregates produced in the UK). However, production of ancillary limestone during actual mining of fluorspar was subject to the Levy.

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This commodity profile was produced by the  
British Geological Survey (2011).

It was compiled by Tom Bide with the assistance of  
Gus Gunn, Teresa Brown and Debbie Rayner.

This report is one of a series of Commodity Profiles  
available to download free-of-charge from  
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