

NSW DEPARTMENT OF **PRIMARY INDUSTRIES**

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FLUORITE

Potential and Outlook

Significant resources of fluorite are present in the large tailings dumps from lead-zinc mining at Broken Hill, particularly at the former Zinc Corporation mine (Figure 10).

These tailings contain up to 3% fluorite, which was one of the gangue minerals of the lead–zinc–silver ore. In the early 1960s, the Zinc Corporation Ltd studied the feasibility of removing the fluorite as part of the processing stream, and also of extracting the fluorite from the tailings, but found it uneconomic (MacNevin & Dawood 1973). Zinc Corporation Ltd apparently also found it difficult to extract fluorite from the tailings to meet acidspar specifications. If fluorite extraction became viable, it may also be possible to recover other materials, such as garnet.

At Doradilla, near Bourke (Figure 10), significant fluorite occurs in copper–gold–tin skarn. Fluorite and wollastonite could be major by-products of any future mining operation and there is a possibility that the deposit could be mined for these minerals alone.



Nature and Occurrence

Fluorite (CaF₂), is virtually the only fluorine mineral of commercial significance. When mined it is usually called fluorspar. Another mineral, cryolite (Na₃AlF₆), was important last century for the production of soda, alum and aluminium sulphate, and also in production of aluminium, but the only known source, in Greenland, has been exhausted. Most cryolite now used is manufactured.

Fluoroapatite, the major phosphate-bearing mineral in sedimentary phosphate deposits, is a major potential source of fluorine. (Commercially produced phosphates may contain up to 3–4% fluorine.)

Fluorite occurs in a wide range of geological environments. The most commercially important deposit types include: hydrothermal veins and stockworks associated with felsic igneous rocks; stratiform replacement deposits in carbonate rocks; skarns and other contact metamorphic rocks; at the margin of carbonatite and alkali igneous rock complexes; and residual deposits in the regolith (Fulton & Montgomery 1994; Harben & Kuzvart 1996). Fluorite also occurs as a gangue mineral in some base metal deposits (e.g. Mississippi Valley type deposits). These consist of veins or replacement bodies and cavity fillings of fluorite, carbonates, quartz and silver–lead– zinc mineralisation in carbonate sequences.

Other deposit types (for fluorine) of lesser economic significance include pegmatites and lacustrine sedimentary deposits (e.g. Piancino in Italy).

World production of fluorite in 2004 was almost 5 Mt (Table 10) (Miller 2005). World trade in fluorite is

Table 10. World fluorite production 2004

| Country | Production (Mt) | Deposit Types |
|-----------------------|-----------------|--------------------------------|
| China | 2.70 | Veins/replacement |
| Mexico | 0.75 | Veins/replacement/ tailings |
| Mongolia | 0.27 | Uncertain |
| South Africa | 0.24 | Veins/stockworks |
| Russia | 0.17 | Uncertain |
| Others | 0.80 | Unknown |
| Total | 4.93 | |
| Source: Miller (2005) | | |

dominated by China, which is also the world's largest exporter. Other significant producers include Mexico, Mongolia and South Africa. Although the nature of the deposits in some major producing countries is uncertain, it is clear that large quantities are produced from vein and replacement deposits and, in one notable instance (Chihuahua, Mexico), significant amounts are recovered from base metal mine tailings.

Main Australian Deposits

There is little or no specific production of fluorite in Australia. Most known deposits are of insufficient size to warrant development.

A large, high-grade fluorite deposit at Speewah, in the eastern Kimberley region of Western Australia, is the subject of a proposal by Mineral Securities Ltd to produce fluorspar concentrate for the export market. The deposit, which contains resources of 4.68 Mt at 22.65% CaF₂, consists of large veins within a complex system of intersecting breccia zones (Fetherston 2002). This project has yet to begin production.

New South Wales Occurrences

There are 67 recorded occurrences of fluorite in New South Wales (Ray et al. 2003) — based on a compilation of fluorite occurrences in New South Wales prepared by MacNevin and Dawood (1973).

There are several small silver–lead deposits south of Yass (Figure 10) in which fluorite is a major gangue mineral. Barite is also a common gangue mineral in those deposits (see chapter on barite). The area contains some of the largest bodies of limestone in the state, and the occurrence of several silver–lead deposits associated with carbonate-bearing sequences is suggestive of Mississippi Valley type deposits. None of the (New South Wales) areas has been systematically explored for fluorite.

Another cluster of small fluorite deposits occurs in the Thackaringa area, southwest of Broken Hill (Figure 10) (see chapter on garnet). A series of discontinuous lenses of quartz–fluorite rock with Broken Hill type base metal mineralisation and calcsilicate minerals occurs over an area of about 3 km by up to 100 m, within the Great Vugh retrograde schist zone. Although only small deposits of fluorite have been found so far, there is significant potential for large deposits (Barnes 1988).

Much larger deposits of fluorite occur at Doradilla, near Bourke (Figure 10), where fluorite occurs as gangue to skarn-type copper–gold–tin mineralisation. The zone of mineralisation at Doradilla is up to 16 km long, and contains varying proportions of fluorite wollastonite and other skarn minerals. The calcsilicate zone averages 50 m to 80 m wide and has been proven to depths of at least 200 m. Weathering in this area has been intense, and may have degraded the upper 50 m of the deposit.

Some large dumps of tailings from lead-zinc-silver mining at Broken Hill, particularly at the former Zinc Corporation mine at the southern end of the Broken Hill Line of Lode have potentially significant resources of fluorite. These tailings contain up to 3% fluorite, which was a common gangue mineral in the lead-zinc ore. Attempts in the early 1960s to extract fluorite from the tailings on a commercial basis were unsuccessful (MacNevin & Dawood 1973).

Possible Mississippi Valley type mineralisation has been discovered at Wonowinta or Blue Mountain, west of Cobar, in poorly exposed Early Devonian Cobar Supergroup rocks. Although fluorite is not known to occur there, the discovery indicates potential for a type of deposit that globally commonly contains fluorite.

Applications

The major use for fluorite is as high-grade material, known as acid-grade fluorspar or acidspar. This is used as feedstock in the production of hydrofluoric acid, which is a starting point for numerous fluorinebased chemicals, particularly chlorofluorocarbons (CFCs), which are used mainly in refrigeration and as propellants, and of synthetic cryolite used in aluminium production (Table 11). About two-thirds of fluorite production is consumed in these applications, and about half the remainder is used in steelmaking.

Environmental concerns about the effect of CFCs on the ozone layer have seen the development of substitutes, which are hydrochlorofluorocarbons (HCFCs) and which contain more fluorine than CFCs. Consumption of CFCs has declined markedly. Substitute materials in slag conditioning include borates, olivine, dolomite and soda ash.

Economic Factors

The phaseout of chlorofluorocarbons (CFCs) resulted in a decrease of over 30% in global fluorite production between 1989 and 1994. Production has subsequently increased because of the development of more environmentally acceptable substitutes for CFCs.

In recent years, substantial cuts in Chinese export quotas have resulted in short supplies and rising prices (Miller 2005). This is providing opportunities for existing producers to increase production and develop new mines.

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| Table 11. Main uses of fluorite | | | |
|---------------------------------|---|---|--|
| Grade | Applications | Specifications | |
| Acid grade | Source of HF; CFCs; refrigerants; propellants; cryolite for Al production | 97% CaF ₂ , <1.5% SiO ₂ ,0.03–0.1% S, 100 mesh grainsize | |
| Ceramic grade | Opacifier in ceramics; enamels; welding rod coatings | 85–96% CaF ₂ , 2.5–3% SiO ₂ , <0.12% Fe ₃ O ₄ | |
| Metallurgical | Slag conditioning | 60% CaF ₂ , <0.3% sulphide, <15% SiO ₂ ,<15% fines | |
| Source: Harben (1999) | | | |