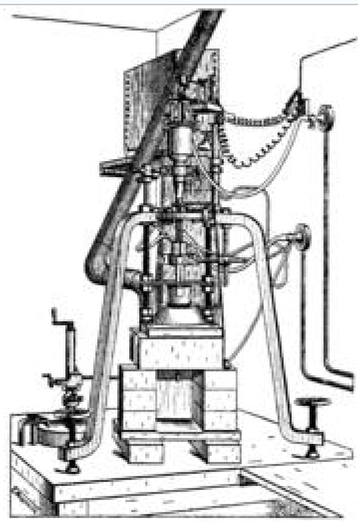
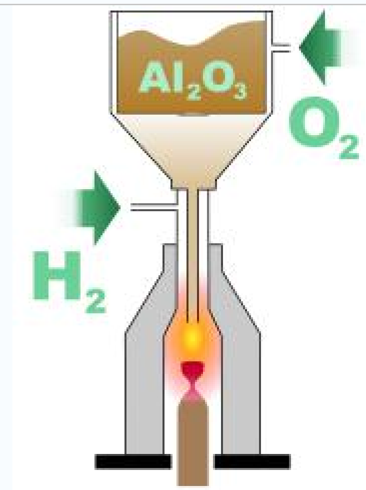
Verneuil Crystal Growth

The **Verneuil process**, also called **flame fusion**, is a method of manufacturing synthetic **gemstones**, developed in **1902** by the **French** chemist **Auguste Verneuil**. It is primarily used to produce the **ruby** and **sapphire** varieties of **corundum**, as well as the **diamond simulants rutile** and **strontium titanate**. The principle of the process involves melting a finely powdered substance using an **oxyhydrogen flame**, and crystallising the melted droplets into a **boule**. The process is considered to be the founding step of modern industrial **crystal growth** technology, and remains in wide use to this day. **(MTI still uses this method to grow SrTiO3 crystal)**



A sketch of an early furnace used by Verneuil to synthesise rubies using the Verneuil process



A simplified diagram of the Verneuil process

History

Since the time of the **alchemists**, there have been attempts to synthetically produce precious stones, and ruby, being one of the five highly prized **cardinal gems**, has long been a prime candidate for synthesis. In the **19th century**, those attempts started to bear fruit, with the first ruby produced by melting two smaller rubies together in **1817**, and the first microscopic crystals created from alumina (**aluminium oxide**) in a laboratory in **1837**. By **1877**, chemist **Edmond Fremy** had devised an effective method for commercial ruby manufacture by using molten baths of alumina, yielding the first gemstone-quality synthetic stones. The **Parisian** chemist Auguste Verneuil collaborated with Fremy on developing the method, but soon went on to independently develop the flame fusion process, which would eventually come to bear his name.

One of Verneuil's sources of inspiration for developing his own method was the appearance of synthetic rubies sold by an unknown **Genevan** merchant in **1880**. These "Geneva rubies" were dismissed as artificial at the time, but are now believed to be the first rubies produced by flame fusion, predating Verneuil's work on the process by 20 years. After examining the "Geneva rubies", Verneuil came to the conclusion that it was possible to recrystallise finely ground aluminium oxide into a large gemstone. This realisation, along with the availability of the recently developed oxyhydrogen torch and growing demand for synthetic rubies, led him to design the Verneuil furnace, where finely ground purified alumina and **chromium oxide** were melted by a flame of at least 2000 °C (3,600 °F), and recrystallised on a support below the flame, creating a large crystal. He announced his work in 1902, publishing details outlining the process in **1904**.

By 1910, Verneuil's laboratory had expanded into a 30 furnace production facility, with annual gemstone production by the Verneuil process having reached 1,000 kg (2,205 lb) in **1907**. By **1912**, production reached 3,200 kg (7,100 lb) , and would go on to reach 200,000 kg (440,000 lb) in **1980** and 250,000 kg (550,000 lb) in 2000, led by **Hrand Djevahirdjian**'s factory in **Monthey**, **Switzerland**, founded in **1914**. The most notable improvements in the process were made in **1932**, by **S. K. Popov**, who helped establish the capability for producing high-quality sapphires in the **Soviet Union** through the next 20 years. A large production capability was also established in the **United States** during **World War II**, when European sources were not available, and jewels were in high demand for their military applications.

The process was designed primarily for the synthesis of rubies, which became the first gemstones to be synthetically produced, thanks to the efforts of Fremy and Verneuil. However, the Verneuil process could also be used for the production of other stones, including sapphire, which simply required **ferric oxide** to be substituted for chromium oxide, as well as more elaborate ones, such as **star sapphires**, where titania (**titanium dioxide**) was added and the boule was kept in the heat longer, allowing needles of **rutile** to crystallise within it. In **1947**, the **Linde Air Products** division of **Union Carbide**, pioneered the use of the Verneuil process for creating such star sapphires, until production was discontinued in **1974** due to overseas competition.

Despite some improvements in the method, the Verneuil process remains virtually unchanged to this day, while maintaining a leading position in the manufacture of synthetic corundum and **spinel** gemstones. Its most significant setback came in **1917**, when **Jan Czochralski** introduced the **Czochralski process**, which has found numerous applications in the **semiconductor industry**, where a much higher quality of crystals is required than the Verneuil process can produce. Other alternatives to the process emerged in **1957**, when **Bell Labs** introduced the **hydrothermal process**, and in **1958**, when **Carol Chatham** introduced the **flux process**.

One of the most crucial factors in successfully crystallising an artificial gemstone is obtaining highly pure starting material, with at least 99.9995% purity. In the case of manufacturing rubies or sapphires, this material is alumina. The presence of **sodium** impurities is especially undesirable, as it makes the crystal **opaque**. Depending on the desired colouration of the crystal, small quantities of various **oxides** are added, such as chromium oxide for a red ruby, or ferric oxide and titania for a blue sapphire. Other starting materials include titania for producing rutile, or titanyl double **oxalate** for producing strontium titanate. Alternatively, small, valueless crystals of the desired product can be used.

This starting material is finely powdered, and placed in a container within a Verneuil furnace, with an opening at the bottom through which the powder can escape when the container is vibrated. While the powder is being released, **oxygen** is supplied into the furnace, and travels with the powder down a narrow tube. This tube is located within a larger tube, into which **hydrogen** is supplied. At the point where the narrow tube opens into the larger one, **combustion** occurs, with a flame of at least 2000 °C (3,600 °F) at its core. As the powder passes through the flame, it melts into small droplets, which fall onto an earthen support rod placed below. The droplets gradually form a **sinter** cone on the rode, the tip of which is close enough to the core to remain liquid. It is at that tip that the **seed crystal** eventually forms. As more droplets fall onto the tip, a **single crystal**, called a *boule*, starts to form, and the support is slowly moved downward, allowing the base of the boule to crystallise, while its cap always remains liquid. The boule is formed in the shape of a tapered cylinder, with a diameter broadening away from the base and eventually remaining more or less constant. With a constant supply of powder and withdrawal of the support, very long cylindrical boules can be obtained. Once removed from the furnace and allowed to cool, the boule is split along its vertical axis to relieve internal pressure, otherwise the crystal will be prone to fracture when the stalk is broken due to a vertical **parting plane**.

When initially outlining the process, Verneuil specified a number of conditions crucial for good results. These include: a flame temperature that is not higher than necessary for fusion; always keeping the melted product in the same part of the oxyhydrogen flame; and reducing the point of contact between the melted product and support to as small an area as possible. The average commercially produced boule using the process is 13 mm (0.5 in) in diameter and 25 to 50 mm (1 to 2 in) long, weighing about 125 carats (25 g). The process can also be performed with a custom-oriented seed crystal to achieve a specific desired **crystallographic orientation**.

Crystals produced by the Verneuil process are chemically and physically equivalent to their naturally occurring counterparts, and strong magnification is usually required to distinguish between the two. One of the telltale characteristics of a Verneuil crystal is curved growth lines formed as the cylindrical boule grows upwards in an environment with a high **thermal gradient**; the equivalent lines in natural crystals are parallel. Another distinguishing feature is the common presence of microscopic gas bubbles formed due to an excess of oxygen in the furnace; imperfections in natural crystals are usually solid impurities.

[**edit**]

References

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