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Usage of vermiculite as a high-temperature insulating refractory material

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Abstract

Vermiculite, a hydrated Mg/Al/Fe silicate mica-like clay mineral with a laminate structure. Vermiculite is a very versatile material. It has a remarkable ability to expand to many times its original volume (exfoliation) when heated (>300°C). The majority of applications call for vermiculite in its exfoliated form, and it has a wide range of applications that take advantage of its significant properties such as low bulk density, low thermal conductivity, odor-free, chemical inertness, easy handle and fire resistance. These properties make vermiculite a promising material for use as high-temperature insulating refractory material in the metallurgical industry. The service (working) temperature of vermiculite-based refractories is about 1100-1150 °C. In order to increase the working temperature and to produce a wide range of vermiculite-based refractory products, refractory binders and fillers (e.g. alumina cement, fire clays etc.) are added to the lightweight vermiculite. In this paper, the application of vermiculite as a high temperature insulating refractory material was mentioned.

Keywords: Vermiculite, High-temperature, Insulating refractory material

Vermikülitin yüksek sıcaklık refrakter yalıtım malzemesi olarak kullanımı

Özet

Vermikülit, laminar bir yapıya sahip hidratlanmış Mg / Al / Fe silikatlı mika benzeri bir kil mineralidir. Vermikülit çok yönlü bir malzemedir. Isıtıldığında (>300°C) orijinal hacminin birçok katına kadar genişleme yeteneğine sahiptir. Vermikülit minerali düşük kütle yoğunluğu ve ısı iletkenlik, kokusuz olması, kimyasal inertlik, kolay tutuşma ve yangına dayanıklılık gibi önemli özelliklerinden yararlanılan geniş bir uygulama alanına sahiptir. Bu özellikler, vermikülitin metalurji endüstrisinde yüksek sıcaklıkta yalıtkan refrakter malzeme olarak kullanılmak üzere uygun bir malzeme olmasını sağlar. Vermikülit bazlı refrakterlerin servis (çalışma) sıcaklığı yaklaşık 1100-1150 °C'dir. Çalışma sıcaklığını arttırmak ve çok çeşitli vermikülit bazlı refrakter ürünler üretmek için, hafif vermikulite refrakter bağlayıcılar ve dolgu maddeleri (örn. alümina çimento, ateş kili, vb.) ilave edilir. Bu yazıda vermikülitin yüksek sıcaklıkta yalıtkan refrakter malzeme olarak kullanılmasından kısaca bahsedilmiştir.

Anahtar Kelimeler: Vermikülit, Yalıtkan refrakter malzeme, Yüksek sıcaklık

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1. Introduction

No high-temperature operation can go without heat management especially, in this 'endless era' of rising energy costs. The solution is of course, refractories and typically speaking, insulating refractories. Production and utilization of high-temperature heat insulating materials make it possible to lower the consumption of material in thermal machines, to reduce by 9-10 times in the weight of the furnaces. Moreover, they are used in order to cut inefficient heat release into the environment and to decrease by 10-15 times the total consumption of fuel in continues furnaces and by 45% or more in bath furnaces. In other words, heat-insulating materials used as additions to mixtures with high porosity provide an effective mean of reducing the apparent density and improving the demand for efficient up to date heat insulating materials has become urgent in the development of ladle metallurgy [1-3].

Vermiculite is a naturally occurring group of hydrated Al/Fe/Mg silicates (mica-like) mineral with a laminate structure with light brown/grey/gold in color. Moreover, vermiculite is a very versatile mineral and it has remarkable properties such as low-density, odor-free, inertness, ease of handling, low thermal coefficient, good acoustic and thermal insulation, absorption capacity, non-combustion material, refractory nature, and is also fire resistant. It is a pebble-like material ranging in size from 2-10 mm in diameter that mined, pulverized and heated to above 300°C in order to exfoliate or expand in size. The majority of applications call for vermiculite in its exfoliated form. Low density and thermal conductivity, as well as a high melting temperature, make vermiculite a promising material for use as a filler in producing heat insulating refractory materials [1,4].

2. Heat insulating refractory materials (HIRM)

The increasing demand for energy saving leads to the development of increasingly sophisticated thermal insulation devices operating at high temperature. Insulations are defined as those materials or combinations of materials, which retard the flow of heat energy by performing one or more of the following functions:

- Conserve energy by reducing heat loss or gain.
- Control surface temperatures for personnel protection and comfort.
- Facilitate temperature control of process.
- Prevent vapor flow and water condensation on cold surfaces.
- Increase operating efficiency of heating/ventilating/cooling, plumbing, steam, process and power systems.
- Found in commercial and industrial installations.
- Prevent or reduce damage to equipment from exposure to fire or corrosive atmospheres.
- Assist mechanical systems in meeting criteria in food and cosmetic plants.
- Reduce emissions of pollutants to the atmosphere.

The temperature range within which the term "thermal insulation" will apply, is from -75°C to 815°C. All applications below -75°C are termed "cryogenic", and those above 815°C are termed "refractory". To be a good insulating refractory material they must have the following properties:

- Low thermal conductivity.
- High porosity.

- Low permeability.
- Withstand the heat of at which they are used.
- Must not shrink or react chemically with the material with which they are in contact during use.
- Mechanically strong enough to bear the load of the structure.

Thermal conductivity (i.e. the time rate of steady state heat flow through a unit area of a homogeneous material induced by a unit temperature gradient in a direction perpendicular to that unit area) porosity, and permeability are the most important properties to evaluate the insulating refractory materials. Most of the produced heat insulating materials are manufactured based on $\text{Al}_2\text{O}_3\text{-SiO}_2$ with other additives e.g CaO, MgO, iron oxides, alkali materials, TiO_2 , etc. The lower volume weight of the material, the lower is its thermal conductivity. These materials have their actual porosity of less than 45% by volume. To increase the porosity of materials many techniques and processes like the addition of burning-up compounds, volatile substances, light-weighted compounds and air foaming-up could be applied in industrial scale. Moreover, the insulating refractory material (esp. shaped, e.g. firebrick) should have enough pore space (to reduce thermal conductivity; uniformly small sized pores distributed preferred) and at the same time cellular in texture. The cellularity of the firebrick texture could be introduced by many techniques. These techniques includes:

- The addition of a combustible substance (e.g. sawdust, paper, etc.) or volatile compound (e.g. naphthalene)
- Using minerals or substances which themselves have open texture or expand and open up on heating (e.g. vermiculite, raw diatomite etc.)
- Aeration
- Chemical bloating (done by using Al powder in combustion with NaOH solution)
- Putting foaming agents in the mixture of the brick [5-7].

In other words, heat-insulating materials used as additions to mixtures with high porosity provide an effective means of reducing the apparent density and improving the refractory properties of components manufactured. Materials of a natural occurrence — vermiculite, diatomite, infusorial earth, perlite, etc. are used as porous fillers.

We could categorize insulating refractory materials in two general groups; namely shaped insulating materials (obtained by deliberate creation of pores in the material) and fibrous refractory materials (produced from the melt or by chemical means). The fibrous refractory materials have many advantages over the shaped materials such as low thermal conductivity, low specific heat capacity, high resistance to vibration and thermal shock, and low density. On the other hand, the shaped insulating materials have advantages in terms of price, mechanical strength, chemical inertness and gas permeability [6].

As the refractory range of insulation is approached, fewer materials and application methods are available. High-temperature materials are often a combination of other materials or similar materials manufactured using special binders. The materials generally used are: calcium silicate, cellular glass, cement, ceramic fibers, glass fibers, mineral fiber, etc. Insulation materials reduce heat flow in linings, and thus they limit the transfer of heat conductivity, convection or both [8]. A vermiculite heat insulating brick is shown in Figure 1.

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Figure 1. Vermiculite-heat insulating brick [12]

3. Vermiculite, properties and its usage as HIRM

As we mentioned before, vermiculite is a group of hydrated Al/Fe/Mg silicates (mica-like) mineral with a laminate structure. Moreover, it is a very versatile mineral and it has remarkable properties such as low-density, odor-free, inertness, ease of handling, low thermal coefficient, good acoustic and thermal insulation, absorption capacity, non-combustion material, refractory nature, resilience to heat, and is also fire resistant. These properties render vermiculite a promising material for fabrication of heat insulating materials suitable for use at high temperatures. The majority of applications call for vermiculite in its exfoliated (expanded) form.

Expanded vermiculite (Figure 2) used as a lightweight porous filler provides superior heat-insulating properties. Expanded vermiculite, owing to its numerous useful properties, has found wide application in construction, metallurgy, etc. In other words, the expanded vermiculite, owing to its unique properties – low bulk density, low heat conductivity, relatively high melting point, chemical inertness, endurance, and environmental safety – can be used as a filler for heat-insulating materials. Heat insulators based on expanded vermiculite can be used in thermal power units with the hot-wall temperature not exceeding 1150°C as a replacement for lightweight chamotte components and fibrous heat insulators.



Figure 2. Expanded Vermiculite [13]

Further efforts for its development and applications are made by specialized research centers under the auspices of the international Vermiculite Association with its headquarters (Chicago, U.S.), the European Affiliated Branch (Lincoln, UK) and Ural Research and Design Institute for Building Materials (Ural NIISTromproekt, Chelyabinsk, Russia). The high thermal stability of expanded vermiculite owing to its ability to relax temperature stress during heating makes possible its use for refractory linings in thermal power units with thermal cycling regimes. In addition, the use of expanded vermiculite as a light-weight porous filler for production of heat-insulating materials makes it possible to ensure high heat-insulating properties not only due to their high porosity, but also due to the capacity of the surface of this material for reflecting heat radiation. [1, 2, 9].

United States (Libby and Enoree Mines), South Africa (Palabora), Russia, China and Zimbabwe has the biggest resources of vermiculite in the world. A company in Turkey continued development of the country's first vermiculite mine in Sivas in central Turkey. Although the date of full production was not yet determined, the first-year production is expected to be about 5,000 tons from a total reserve of 7 million tons, of which more than one-half was considered high quality [4].

Aforementioned, vermiculite has a wide range of uses as heat and sound insulation, packaging, coating and fire protection material in refractory, construction and many other industries. The special feature responsible for the technological value of vermiculite is its ability, when heated to above 300 °C, to expand and thus to convert to an efficient heat-insulating material with low density. The density of expanded vermiculite depends on the quality of the raw material, its fractional composition, and the heating method employed [4, 9]. The physicochemical properties of vermiculite are shown in Table 1.

Table 1. Properties of vermiculite

Formula	$4.5\text{H}_2\text{O} \cdot \text{MgO}_{0.3} - 0.4 (\text{Al}_2\text{Si}_6)(\text{Mg, Fe, Al})_6\text{O}_{20}(\text{OH})_4$
Thermal Conductivity (W/m.K)	0.04 – 0.12
Density (Expanded Vermiculite) (Kg/m ³)	50 - 150
Service Temperature (°C)	1100 - 1150
Melting Point (°C)	1240 - 1430

On the other hand, as a disadvantage, particles of expanded vermiculite are fragile with low strength. The compressive strength in a direction perpendicular to the cleavage plane is marginal, and the elasticity of particles is minimum. In a direction parallel to the cleavage plane, the compressive strength is 50 kPa. Raising the calcination temperature above 700°C causes a decrease in the strength of expanded vermiculite (hydro phlogopite) because of structural changes in the mineral. The strength of expanded vermiculite (in view of the fragility of its particles) is evaluated in terms of brittleness, what characterizes the strength of the material in the bulk rather than the strength of its individual particles.

Expanded vermiculite is produced as a granular loose fill dry (mixed with fillers and binders) and used in the production of insulation shapes which are typically produced using finer grades of the mineral. High alumina cement and exfoliated vermiculite can be combined with other aggregates such as expanded shale, clay and slate to produce refractory/insulation concrete and mortars. For refractory and high-temperature insulation, it is normally bonded with alumina cement, fire clays and silicates to produce a wide range of vermiculite products, which, depending on the type and application can withstand temperatures of up to 1100-1150 °C. Simply, heat-insulating vermiculite products based on argillaceous binders consist of expanded vermiculite (a lightweight filler), refractory or high-melting (red) clay, possibly with tripolite additive, diatomite (a binder), and nonplastic refractory material: chamotte, magnesite powder, corundum waste (a refractory filler). By varying the content of the three main components and the material composition of the binder and the refractory filler, high-temperature heat-insulating materials have been obtained. The type of refractory products made using vermiculite are pre-fired clay bonded insulation firebricks; castable high alumina concretes for backup insulation; high alumina bonded bricks, slabs and special shapes; silicate bonded insulating shapes and molded products. [10, 11].

From among the wide range of heat-insulating materials based on expanded vermiculite, only those with a refractory matrix can find the application at temperatures exceeding 1000°C. High-temperature heat-insulating materials with a ceramic refractory matrix, conventionally called ceramic vermiculite materials, have been under development mainly in Russia (former USSR) and U.S.

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starting from the late 1930s. Until the 1960s, the research was mainly academic; the first reports on practical applications appeared in the mid-1960s. A wide range of vermiculite-based heat-insulating materials using mineral binder fabrication technologies has been developed. What's more, ceramic composite vermiculate plates could be used to line the hot walls of tunnel-type and ring furnaces, the bottom of tunnel kiln wagons, the walls and the arch of glass-melting furnaces, the hearth of electrolyzers for the production of metallic aluminum, and the arch of glaze kilns. The aluminum-making, petrochemical and petroleum-refining industries are among the major potential users of these products [1-3].

In previous studies [1, 2], the production technology and composition of high-temperature heat-insulating materials based on vermiculite have been developed in Russia, Borovichi Refractory Works. In this factory, using these materials makes it possible to lower material consumption in thermal machinery, reduce inefficient heat losses, and decrease by 10 – 15 times the total fuel consumption in continuous furnaces and by more than 45% in batch furnaces. The thermal conductivity of the developed refractory material is comparable to fibrous heat insulating materials. The main properties of the developed refractory material for actual service conditions are shown in Table 2.

Table 2. Properties of the developed vermiculite based HIRM

Density (Not Expanded) (kg/m ³)	400-600
Bending Strength (N/mm ²)	0.49-0.56
Thermal Conductivity (650° C W/m.K)	0.11-0.18
Thermal Conductivity (350 ° C W/m.K)	0.09-0.16
Service Temperature (°C)	1100-1150

4. Conclusion

Expanded vermiculite obtained by calcination from raw vermiculite ore or its concentrates exhibits a range of unique properties: low bulk density, low heat conductivity, and comparatively high melting point; among its other benefits are chemical inertness, endurance, and environmental safety. All these appealing features make vermiculite a promising material for use as a filler in the production of heat-insulating components.

Based on expanded vermiculite, high-temperature heat-insulating materials were developed, with quite satisfactory performance characteristics in Russia. The heat conductivity of vermiculite-based components does not differ much from that of fibrous heat-insulating materials. The physicochemical characteristics of new high-temperature heat-insulating materials based on vermiculite can be used in thermal power plants with the hot-wall temperature not exceeding 1150°C as an alternative to lightweight chamotte components and fibrous heat insulators. The only disadvantage of vermiculite-based material is the low mechanical strength. It should be considered in under-load applications in metallurgical processes. Vermiculite-based products, will undoubtedly rank high in the near future in the area of high-temperature heat-insulating materials.

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