

Aluminosilicate Refractory Clay Minerals

D. A. Jarvis

For anyone who really wishes to start at the very beginning, the story of the formation, discovery and exploitation of aluminosilicate clay minerals, which originally formed the basis for the start of the early refractories industry goes back an incredibly long way in time.

It starts in fact with the so called "Big Bang" which is estimated to have occurred perhaps somewhere around 13,5 billion years ago plus or minus almost a quarter of a billion years either way. The big bang as an initial event itself is estimated to have taken place in a time frame of less than 3 min. The building blocks of the universe were apparently first formed at that point and not only has it been constantly expanding since that moment in time but in fact continues to do so at an increasingly rapid speed even although this is not readily apparent to most people as we live our normal day to day lives.

Creation of elements from the "Big Bang"

In the initial "inflation", the main element which existed appears to have been hydrogen some of which formed helium in nuclear fission which took place at millions of degrees Kelvin.

Perhaps there were also small amounts of lithium and beryllium initially present or rapidly formed. As the gases expanded and cooled stars were formed and these were grouped into different galaxies perhaps by gravitational forces.

The self-destruction of many of these original stars created the other chemical

elements found in nature and distributed them much further afield. This phenomenon is known as nucleosynthesis where the original hydrogen atoms formed helium before some helium atoms themselves fused to form carbon. Some carbon atoms and helium atoms then fused to form oxygen, similarly oxygen atoms fusing with helium formed neon while neon fusing with helium produced magnesium.

As this process then accelerated as in a nuclear reaction it formed all of the known naturally occurring elements in the periodic table including of course aluminium and silicon, which with hydrogen and oxygen

form the basis of kaolinite which is the purest form of aluminosilicate clay mineral.

These original particles and energy are believed to have formed our sun and solar system by core accretion where gravity drew matter together to collapse in on itself. Vapours and gases coalesced and eventually condensed into liquids which froze at least on the surface to then produce solids containing elements, compounds, mixtures, minerals and eventually rocks. If we accept that the Earth itself is slightly less than five billion years old then we may also be able to accept that the initial primary stages of formation of our planet took up about 70–80 % of this period of time.

Our home planet then also underwent subsequent changes in atmosphere, orbit, inclination, size, and shape. These and other geomorphological processes including glaciation following continental drift caused many igneous rocks to break down and be transformed in different ways before being transported many thousands of kilometres from the original source, while some very few, and often very pure, clay minerals were actually transformed hydrothermally in situ

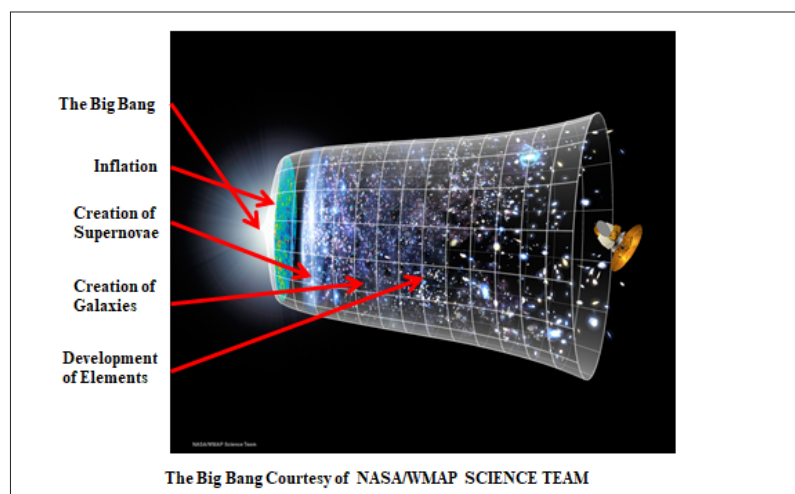


Fig. 1 Creation of elements from the "Big Bang"

David A. Jarvis

E-mail: dajarvis@btopenworld.com

is the longest and the products of mineral transformation from the original igneous and metamorphic rocks are carried down along its whole length depositing soil, clay and silt close to the river banks. This deposition of clay along the rivers banks effectively transforms the Nile valley from desert conditions into conditions suitable to support human habitation.

It is believed that almost 90 % of the permanent population of Egypt of almost 100 million people currently live in close proximity to the river banks. A similar situation exists in other locations around the world such as between the Tigris and Euphrates Rivers where the headwaters are in the mountains of eastern Turkey and western Iran, before both of these rivers eventually reach the Gulf in the marshes near Basra.

The Indus rises in the Himalayas and again flows to the south carrying masses of soil, clay and silt through Pakistan to its wide delta on the Arabian Sea. Even more spectacularly, in China there are three great river systems rising in the west of the country and flowing east to the coast. These are the Yellow River in the north, the Yangtze River which is by far the largest and the Pearl River in the south with an estuary near Hong Kong. Xi'an, which is well known as the site of the terracotta warriors, is on the Yellow River system as is Luoyang which is also active in refractories production from both local and imported raw materials.

China in fact produces around 2 Mt/a of kaolinites with the harder flint clay materials originating in northern China while the now sedimentary kaolinised type granites are found mainly in the south. Gaoling is an area of hills and lakes in Jianxi province south of Shanghai which gives its name to the mineral kaolinite. Clays have been mined here and used to make pottery for thousands of years. A broken ceramic pot found in the area has been dated to around 8000 years old. Around 1700 A.D., a Jesuit missionary is said to have acquired some of the pure white kaolinite from this region and spirited it back along the Silk Road to introduce it to European ceramic manufacturers who were still largely unaware of the use of this type of raw material in ceramics at this time. Many other clay deposits, far too numerous to mention individually and of widely varying quality, are found around

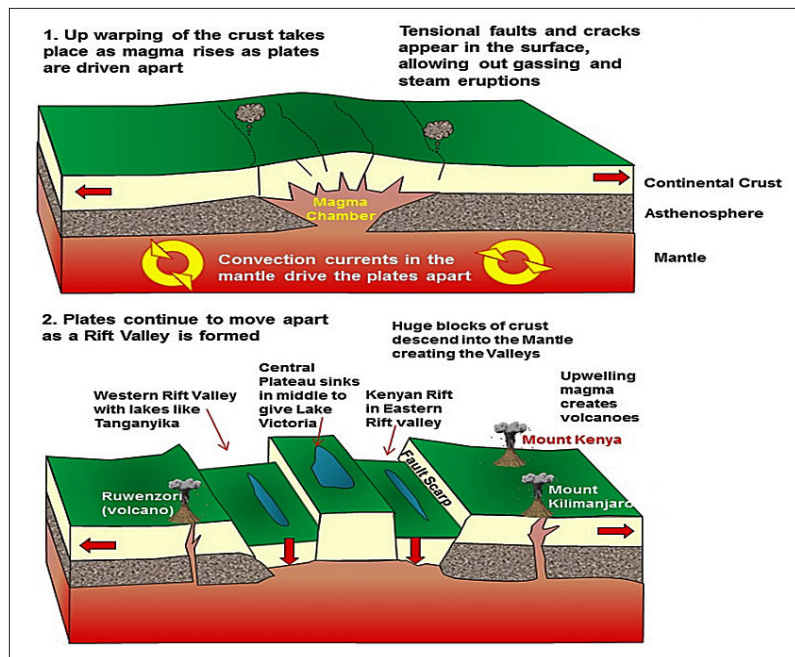


Fig. 3 Formation of the African rift valleys

(Courtesy of Rob Gamesby)

the entire world and most although not all originated in a very similar way to that exemplified above.

It is also interesting to consider that extensive DNA studies appear to indicate that human life is believed to have originated somewhere in the region of the Rift Valley. The "Out of Africa Theory" postulates that people travelled north up the Nile valley, and then split with one branch travelling through the Middle East to northern Europe; the other through river valleys in Asia and then over a land bridge to colonise all the way down the west coast of the Americas to southern Chile with at least one excursion to the east along the Amazon River Valley in

Brazil. Water borne clay particles have obviously played a major role in all this.

The processes of geomorphology may be thought by many people to be fairly self-evident but some researches have gone very much further to quantify them using numerous detailed experiments and mathematics to define the mechanisms involved in some of the aspects of the overall process. Hjulstrom has created a diagram which illustrates that as rocks are broken down and reduced in size into different components of varying diameters, densities and compositions the finer particles as would be expected tend to travel faster and further than the larger denser particles. The rela-

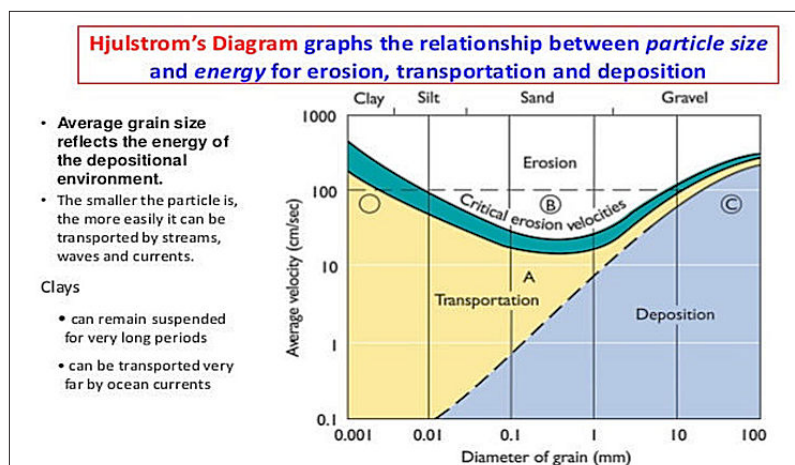


Fig. 4 Hjulstroms diagram

(Courtesy of the Geological Institute Uppsala)

relationship between the various particle properties and the energy required for erosion, transportation and deposition are defined in some detail. One conclusion from the studies is that clay particles can be transported for distances of up to 5000 km from the point where they are originally formed to the point where they may eventually be currently located.

Clay deposits

There are many clay deposits of varying quality around Europe in places as different as the former Czechoslovakia which is rich in kaolin, but poor in bauxite to southern France which is rich in bauxite and poor in kaolin as in the area around Les Baux just

south of Avignon. Many European deposits like some of those in Great Britain are similar to the clay deposits which run down almost the entire eastern seaboard of the USA and sit on a hard base rock such as limestone.

These clay deposits are often overlaid by coal. When these alluvial clay deposits were originally formed plant and animal life thrived in and around them, they all supported the growth of massive ferns, trees and much other vegetation. At some point in time, this was brought down by the forces of nature and the vegetation was transformed into coal on top of a layer of compressed clay. When laid down the layers would have been horizontal with the coal seams up to

perhaps 1 m thick and the clay seams being at least twice that thickness. Today, many of these deposits are both inclined and faulted due to subsequent movement of the rocks and most are also covered with new overburden. This is typical of the very extensive refractory clay deposits in central Scotland. These run from St. Andrews in the north east of Fife to Dumfries which lies to the south west of Ayrshire. These deposits are not completely continuous, but are almost so and even run under the very wide estuary of the River Forth where mines have yielded mainly coal until recently.

When assessed by alumina and silica content as well as impurity levels such as iron content, the quality of the clays varies from fairly low in the north-east to very high in the south-west which also yields bauxitic clay which was at one time exploited by an A. P. Green subsidiary.

Some of the central Scottish clays are very pure having an iron content of about 1 % and containing between 42–44 % alumina. These were the basis of the Scottish firebrick industry which with about 40 companies engaged in production, sent bricks and mortar to many different applications around the world for over 200 years. Sadly, these sites have almost all been closed, demolished and landscaped with one even being turned into an industrial museum. One old site, opened originally in Bonnybridge in 1884, was recently acquired by Magnesita RHI who still manufactures a range of products for the steel industry.

There is an interesting comparison to be drawn between the clay deposits in the north and east of the USA, those in the Midwest and other very different ones on the west coast. In 1816, a waggon train set out from St. Louis heading for California but very soon encountered a fork in the trail. At this location someone had fashioned a large wooden sign with an arrow pointing due south on which they had scrawled "Mexico". After discussing the options, the waggon train turned south and after few days travel came to a land of low rolling hills and lakes which they agreed was a perfect place to create their ideal new settlement.

Further discussion on what to call the new town was brought to a rapid close when the waggon master decided that they would either call it Mexico or someone would

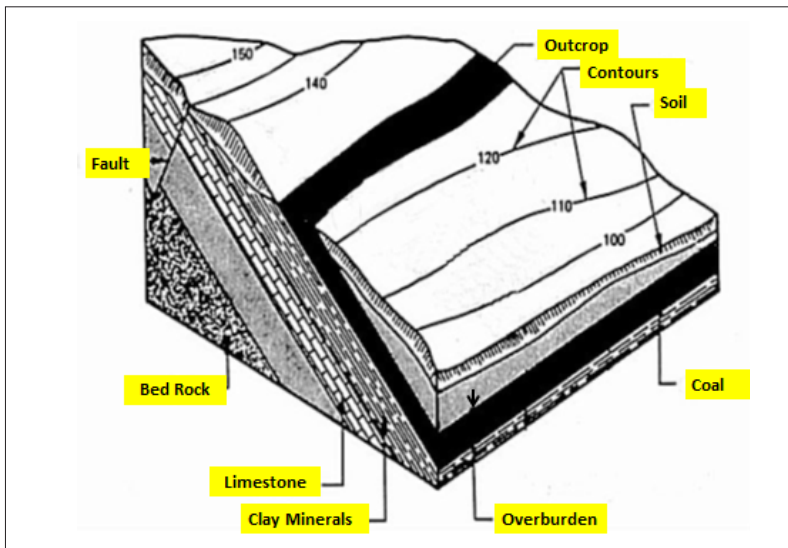


Fig. 5 Stratification of clay deposits

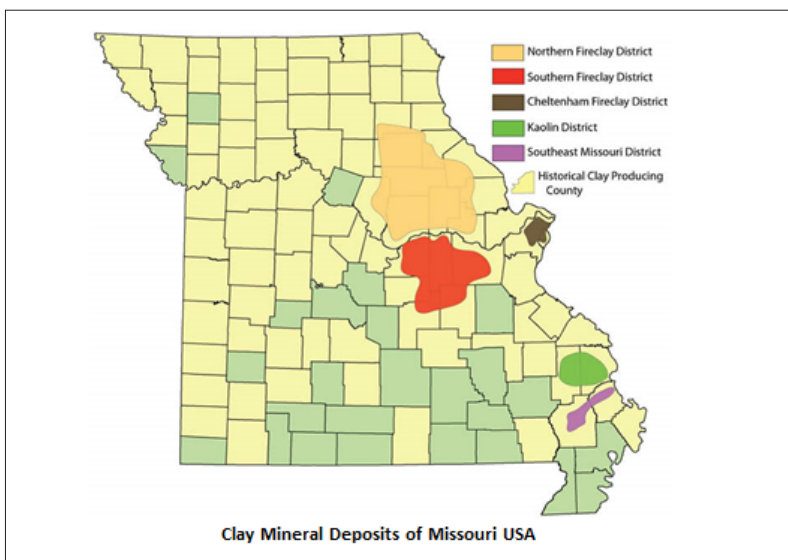


Fig. 6 US Midwest clay deposits (Courtesy of Missouri Dept. of Natural Resources)

have to go all the way back up the trail and change the name on the signpost. It was another 50 years later, before it was discovered that not only had they chosen an ideal area for farming, but that they were sitting on top of one of the biggest deposits of high quality refractory fireclay in the world. Thus were A. P. Green and several other American companies founded in the Midwest.

The United States Geological Survey shows that not only the entire state of Missouri, but most of the surrounding states have extensive rich clay mineral deposits. Arkansas and Tennessee have bauxite, Georgia has kaolin and Kentucky has ball clay, to name only a few examples. In Missouri, while the entire state has clay deposits, the highest quality ones run down the eastern edge of the state from the town of Warsaw in the north through St. Louis to Tomato in the extreme south.

This area coincidentally borders the Mississippi River, although it is perhaps misleading to call it a river rather than a huge river system. The headwaters of the Mississippi are in Wyoming, but the system drains 40 % of the land mass of the USA with tributaries flowing through 37 states. While the great lakes still exist today, the probability was that Missouri, which is relatively close to them, was at one time the site of another vast lake or perhaps more accurately an inland sea where the clays were deposited on the bed. Further south on the river is the Atchafalaya Swamp Basin which covers over 1 million acres in Louisiana. This swamp may be a work in progress with new clay deposits being formed in geological time in a similar manner to that which exists today.

Some clay deposits in California on the west coast, while also being high quality, have however undergone further additional and different transformations. Most of this clay was originally the bed of a very shallow sea off the present West Coast. Continental drift has compressed these deposits between the Pacific and the USA plates into an area which runs for some distance in a north-south direction along the western edge of the San Andreas Fault. This clay has undergone transformation from extreme pressure, but also from high temperature which at one location has created the lone flint clays. These white, very-low iron clays are already effectively pure, calcined, and

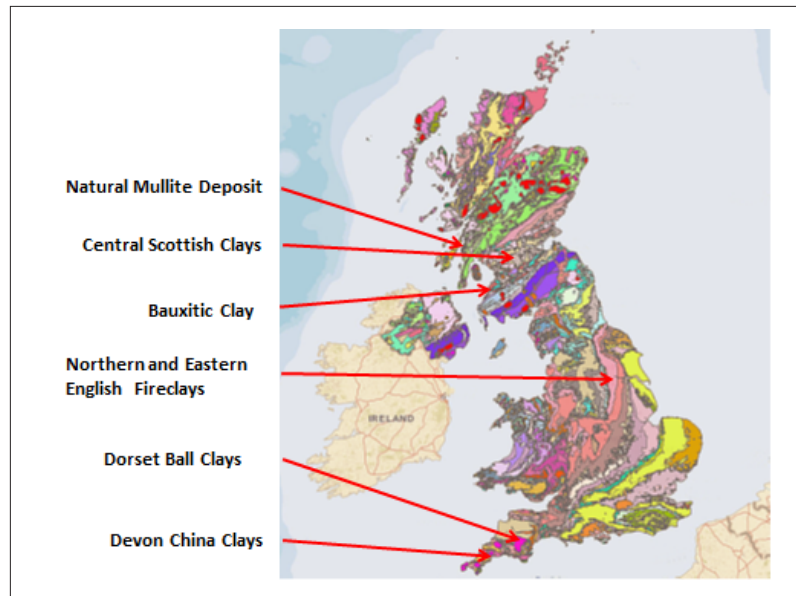


Fig. 7 Clay deposits in Great Britain

(Courtesy of the British Geological Survey)

volume stable kaolinite. This deposit occurs in the foothills of the Sierra Nevada Mountains in the Amador County, adjacent to some quartz deposits which contained most of California's gold before the gold rush of 1849 depleted the state's resources.

Some GB clay deposits are equally interesting with granite being hydrothermally altered in situ in localised areas of Dartmoor in Cornwall to form China clay and ball clays in Devon and Dorset, which were probably hydrothermally transformed at some stage from volcanic ash.

The most unique occurrence however is on the Isle of Mull where a small deposit of mullite has been identified. This is granite which has been hydrothermally altered in situ to kaolinite before being subsequently subjected to temperatures in excess of

1400 °C to transform it into mullite. This is thought to be the only occurrence of mullite in nature and the several adjacent extinct volcanoes surrounding it, including the huge Ardnamurchan with a caldera of more than 5 km in diameter, were almost certainly instrumental in this phenomenon occurring in this very specific and apparently unique locus.

Aluminosilicates

The term kaolinite has been used several times to refer to what is not only the purest form of hydrated aluminosilicate but also sometimes a generic name for other closely related but perhaps not so chemically pure clays occurring worldwide. Pure kaolinite can be represented by the formula $Al_2 \cdot Si_2 \cdot O_3(OH_4)$ and occurs as microcrystal-

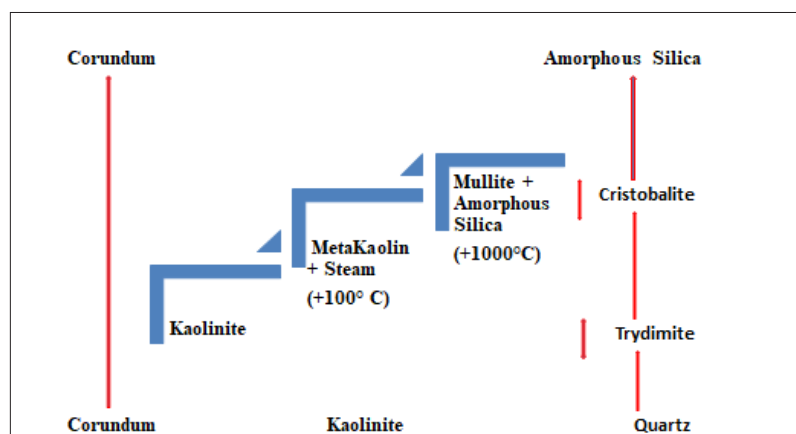


Fig. 8 Transformation of aluminosilicates with rising temperature

Tab. 1 Comparison of raw and fired refractory clays [mass-%]

Component	Raw Missouri Flint Clay	High Calcined Flint Clay	Raw Diaspore Clay	High Calcined Diaspore Clay
Al ₂ O ₃	38,63	44,60	76,21	89,19
SiO ₂	44,42	51,39	3,89	4,46
Fe ₂ O ₃	0,55	0,62	0,98	1,13
TiO ₂	2,12	2,42	3,52	4,03
CaO	0,04	0,43	0,08	0,09
MgO	0,10	0,11	0,06	0,07
Na ₂ O	0,30	0,34	0,79	0,90
K ₂ O	0,12	0,14	0,24	0,27
H ₂ O	13,90	0,00	14,56	0,00
Total	100,18	100,00	100,33	100,14

line plates or grains in compact unshaped masses which as has already been stated are all most likely to have been deposited from suspension in water. Bowen, a Canadian geologist, and his coworker Greig, carried out a substantial series of experiments in 1924 to derive the alumina-silica binary phase diagram. Mixtures of pure corundum (Al₂O₃) and pure quartz (SiO₂) were prepared in multiples of 1 % from 100 % alumina to 100 % silica. These were then heated from ambient to the point at which the mixture was completely liquid, and this temperature for each mixture was designated and plotted as a liquidus line on a graph. The results which they obtained have not been modified much by subsequent experiments although other workers have added considerably to the knowledge of important solid state changes occurring at much lower temperatures. Some of these phase changes are reversible and some not, and are espe-

cially important in compositions very high in silica as they can be accompanied by volume changes.

It can be seen from this and other work that kaolinite, when heated progressively, loses its free water at about 110 °C, and then its water of crystallisation at around 550 °C when it transforms to metakaolin. If heating continues up to a temperature of 1000 °C, the metakaolin dissociates into a spinel phase sometimes referred to as gamma alumina and a type of silica in the form of alpha or beta tridymite. Further heating of the material above 1000 °C, sees the spinel phase transform into mullite in plate-like form, but still with an excess of silica present in the form of tridymite. Heating beyond this temperature to at least 1470 °C, causes the mullite to recrystallise as needles and any excess silica present to become first of all alpha or beta cristobalite and then an amorphous glassy phase.

All aluminosilicate materials, whether natural or synthetic, thus have some mullite present after heating along with other phases depending on the original chemical composition. Natural raw materials of course are likely to have other impurities including iron, lime, magnesia, alkalis and perhaps carbon, and other trace elements which start to complicate the situation by significantly altering the physical properties, and the applications in which the fired product can be used.

This is why today a lot of refractory clays are pretreated by heating to remove water and often by passing under magnets to remove iron, for example after heating. The precalcination also promotes the formation of metakaolin as well as sometimes mullite in the grain which making the clay denser, stronger and much more volume stable, when the end products are subsequently put into use as refractories in industrial applications.

The alumina-silica binary phase diagram still provides good guidance as to where aluminosilicate refractories including those based on clays can best be used in practical applications.

Fired or precast refractories very high in alumina can be used in steel electric arc roof delta sections, where they resist temperature and slag attack or in the reaction domes of chemical reformers, where their high strength helps bear the weight of the catalyst. Fired bricks and shapes very high in silica can be used in glass tank roofs as well as in conventional coke ovens or in the domes of high temperature hot blast stoves in ironmaking.

Refractories containing around 70–85 % alumina can be used in such diverse applications as in rotary kilns in the mineral processing industries or the baths and lower walls of aluminium melting and holding furnaces. In bricks and blocks where the alumina and silica present is all fully converted to mullite these can be used in tunnel kiln roofs because of their high hot strength.

Mark Twain may have had aluminosilicate clay minerals very much in his mind when he claimed that “there are lies, damned lies, and statistics”. The problem being that there are many different types of clay described in different ways by different statisticians. Some of the statistics relate to the very broad categorisation of “Structural”

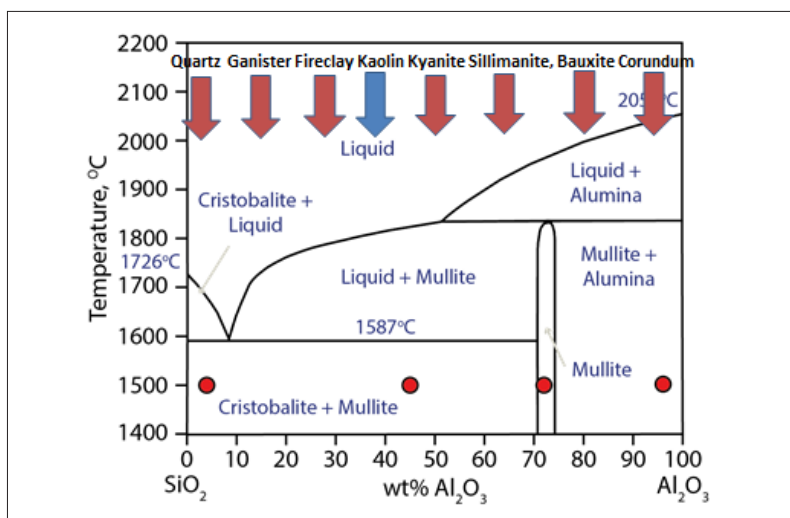


Fig. 9 Aluminosilicate clays and minerals in refractories usage

or "Industrial", some relate to the specific type of clay and some to the many and varied end uses. In USA in the past, some statistics have been omitted from large tables of data because the figures were deemed commercially sensitive while in other locations little current information is available. A US Geological Survey Year Book published in 2004 puts world total production of kaolinite at around 44,5 Mt. If we consider only kaolinite type clays, then China is the largest producer in the world, but has been omitted from some reports because "no reliable estimates were available" and even the figures that are published vary depending on the source.

The US Geological Survey indicates that the USA was a major producer with an output of about 7,7 Mt, where in one year Missouri alone mined about 75 % of the total North American production. European production combined appears to be just less than 10 Mt with Germany the largest single producer with about 47 % of the total European production followed by Turkey, Great

Britain and the Czech Republic respectively. Many producers of fireclay consume their own raw material within their own organisation rather than sell it and many traders source materials from many locations and sell it widely.

One of the largest global organisations producing and selling kaolinite as well as 30 other clay and nonclay minerals is Imerys S.A. It is based in France, but operates from 270 sites in 50 countries on 5 continents. The group has over 18 000 employees and enjoy a turnover of EUR 4,6 billion. Many other large and small miners and traders operate in this specialist area. It appears that however refractory aluminosilicate clays are defined, their production and use continues to be a significant sector in the overall usage of refractories. This is said to be because of the abundance of raw material which is available at economic prices compared to some more exotic refractory materials such as magnesia or zirconia.

Even the substantial beneficiation of the clays to form more stable raw materials

does not change the economics to the point where these materials are priced out of the market. A high or super-duty firebrick with chemical purity, accurate dimensional tolerances, high density, excellent hot strength and good corrosion resistance against impurities in the industrial processes in which it is deployed can still be an extremely cost-effective solution in the production of many basic commodities. These raw materials are not only the basis for dry pressed and tunnel-fired bricks, but also of a wide range of refractory monolithics.

About 80 % of the monolithics used today are in the form of free flowing castables, vibratables or gun mixes and these contain very high proportions of aggregate which is carefully graded in size to achieve maximum packing density in use. Plastic or ramming mixes are also based on graded aggregates, but normally contain a higher proportion of plasticiser to allow the refractory shapes to be moulded or the gunning plastic to consolidate during installation.

As always in refractories engineering, high technology has superceded art, and often machinery superceded manual labour. The outcome is the same: high quality linings, but much faster and more cost-effective solutions for the many important end users.