WOLLASTONITE AND DIOPSIDE FLOTATION

Adilbek Rustemov

Department of Mining and Materials Engineering

McGill University

Montreal, Quebec, Canada

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Abstract

Wollastonite is a calcium inosilicate mineral ($CaSiO_3$) which is used in a variety of industries including ceramic, plastic, painting, pharmaceutical and paper industries. Wollastonite flotation that contains silicate minerals as gangue is challenging and rarely discussed in literature, even though wollastonite beneficiation technologies are more developed and studied than that of diopside.

Diopside is another silicate mineral with composition ($MgCaSi2O_6$). It is a monoclinic pyroxene mineral, which is usually found in solid solutions with hedenbergite and augite in ultramafic igneous rocks. There is a scarce information on diopside beneficiation in general due to probably relatively low industrial importance of this mineral. However, in the recent years, importance of diopside started to grow due to new discoveries of valuable properties of this mineral.

In this study, Design of Experiments (DOE) was used to find optimum wollastonite flotation conditions. Multiple types of collectors have been used in the experiment to analyze direct and indirect relationships between input factors and their effect on output variables. Response Surface Methodology (RSM) has been utilized for analysis and subsequent modelling of the process with three-dimensional contour plots. Six experimental input factors including the dosages of B-400, HT, CA-375, CA-250, R855 and R845 were selected as the main factors. Recovery of wollastonite to sink and recovery of diopside to float have been defined as response variables.

B-400 and R855 showed strong non-selective collecting properties, while CA-375 and CA-250 exhibited highly selective collecting properties. HT and B855 displayed some enforcing behavior in some combinations with CA-250, however acted weakly in other combinations.

Finally, based on the model optimization results, optimum operating conditions have been derived. In order to reach maximum possible recoveries of above 90% collectors CA-375, CA-250 should be used at maximum dosages of 191.4 g/t each, while HT and R845 at the low dosages of 15.7 g/t and 10.1 g/t respectively. B-400 and R855 should not be utilized at all.

Résumé

La wollastonite est un minéral d'inosilicate de calcium (CaSiO3) qui est utilisé dans une variété d'industries, y compris les industries de la céramique, du plastique, de la peinture, pharmaceutique et du papier. La flottation de la wollastonite qui contient des minéraux silicatés sous forme de gangue est difficile et rarement discutée dans la littérature, même si les technologies d'enrichissement de la wollastonite sont plus développées et étudiées que celle du diopside.

Le diopside est un autre minéral silicaté de composition (MgCaSi2O6). C'est un minéral pyroxène monoclinique, que l'on trouve généralement en solutions solides avec l'hédenbergite et l'augite dans les roches ignées ultramafiques. Il existe peu d'informations sur l'enrichissement du diopside en général en raison de l'importance industrielle probablement relativement faible de ce minéral. Cependant, ces dernières années, l'importance du diopside a commencé à croître en raison de nouvelles découvertes de propriétés précieuses de ce minéral.

Dans cette étude, le plan d'expériences (DOE) a été utilisé pour trouver les conditions optimales de flottation de la wollastonite. Plusieurs types de collecteurs ont été utilisés dans l'expérience pour analyser les relations directes et indirectes entre les facteurs d'entrée et leur effet sur les variables de sortie. La méthodologie de surface de réponse (RSM) a été utilisée pour l'analyse et la modélisation ultérieure du processus avec des tracés de contour tridimensionnels. Six facteurs d'entrée expérimentaux comprenant les dosages de B-400, HT, CA-375, CA-250, R855 et R845 ont été sélectionnés comme facteurs principaux. La récupération de la wollastonite pour couler et la récupération du diopside pour flotter ont été définies comme variables de réponse.

B-400 et R855 ont montré de fortes propriétés de collecte non sélectives, tandis que CA-375 et CA-250 ont montré des propriétés de collecte hautement sélectives. HT et B855 ont affiché un certain comportement d'application dans certaines combinaisons avec CA-250, mais ont agi faiblement dans d'autres combinaisons.

Enfin, sur la base des résultats d'optimisation du modèle, des conditions de fonctionnement optimales ont été dérivées. Afin d'atteindre des récupérations maximales possibles supérieures à 90 %, les collecteurs CA-375, CA-250 doivent être utilisés à des doses maximales de 191,4 g/t chacun, tandis que HT et R845 aux faibles doses de 15,7 g/t et 10,1 g/t respectivement. B-400 et R855 ne doivent pas être utilisés du tout.

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Statement of Authorship

I hereby declare that I am the sole author of this master thesis and that I have not used any sources other than those listed in the bibliography and identified as references. I further declare that I have not submitted this thesis at any other institution in order to obtain a degree.

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Introduction

Wollastonite is an industrial calcium metasilicate mineral ($CaSiO_3$), named after William Hide Wollaston (1766-1828), a British Scientist. It is formed by the metamorphism of siliceous limestone at temperatures around 450°C and higher, and usually occurs in regionally metamorphosed high-grade rocks and near igneous contact zones (Kangal, Bulut et al. 2020). Wollastonite has pure formula of $CaSiO_3$ and theoretical composition of 48.3% CaO and 51.7% SiO2, however, in nature Fe, Mg or Mn can substitute for some amounts of Ca and therefore reduce the whiteness & brightness of the mineral (Andrews and Division 1970).

Wollastonite is a fibrous white mineral with needle-like shape (Figure 1), the quality, which makes it valuable mineral in many fields of application like ceramics, plastics, resins, paints, coatings etc. where it is mostly used as a filler material. Its aspect ratio (relation of width to height) can reach up to 20:1 providing high acicularity and strong reinforcing qualities (Swarna, Kota et al. 2003).

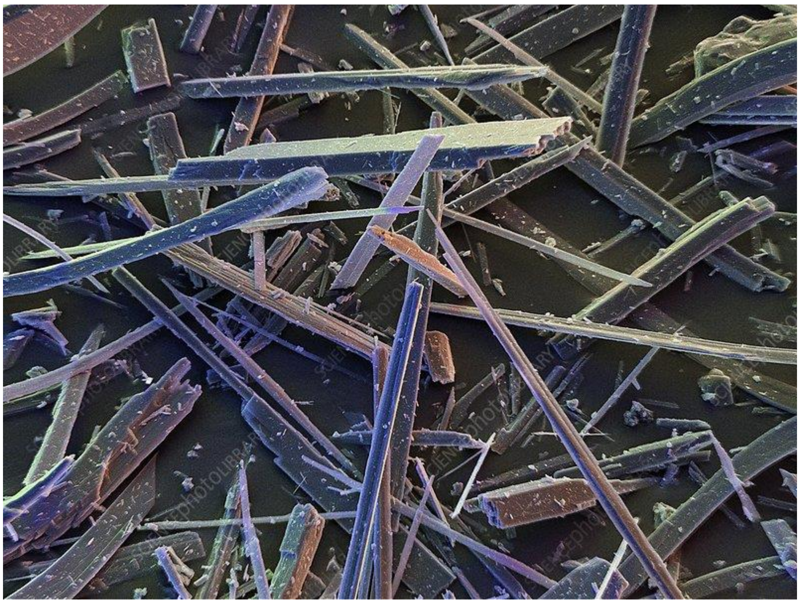


Figure 1. Colored scanning electron micrograph (SEM) of wollastonite (Scharf)

Nowadays, China is the leading producer of wollastonite with an estimated annual production of 890,000 tons in 2019 - up from 750,000 in 2013 (Perry 2012). The second is India with 150,000 tons per year – a fall from its 2013 total of 193,000 tons. Third biggest producer of wollastonite is Mexico with 93,000 tons of annual production – up from 88,000 tons in 2017 and the fourth being the US with an estimated production of 50,000 tons in 2017. Finally, Finland had 11,000 tons in 2018 – up from 10,000 in 2017, Canada - 10,000 tones, down from 11,000 in 2017 and other countries contributed around 6,000 tones with the total global production being 800,000 tons - up from 770,000 tons in 2017.

For example, some wollastonite deposits in USA have been mined for more than 50 years. Currently, there are two companies producing wollastonite — NYCO Minerals Inc. operates a mine in Essex County (New Jersey), and R.T. Vanderbilt Co. Inc. operates a mine in Lewis County (New Jersey). The NYCO deposit contains wollastonite, garnet, and diopside. Some parts of the deposit contain 60% wollastonite. The ore is treated at the Willsboro plant where the garnet is separated by high-intensity magnetic separators. The company also chemically modifies the surfaces properties of some of its wollastonite concentrates to improve their performance and meet various requirements of the consumers. The R.T. Vanderbilt deposit comprise primarily of wollastonite and some amounts of calcite and prehnite and insignificant amounts of diopside. The company process the ore at its Balmat plant where it is milled and air classified (Virta 2001).

There are no reliable estimates of wollastonite reserves for most countries, however, according to US Geological Survey (USGS) large deposits have been identified in China, Finland, India, Mexico, and the US, and medium-sized deposits have been identified in Canada, Chile, Kenya, Namibia, South Africa, Spain, Sudan, Tajikistan, Turkey, and Uzbekistan with an estimated world reserves of 100 million tons (Lopez 2019).

It is important to note, that wollastonite can also be synthesized artificially and there are many ways perform that, however two of them are most common – single step synthesis with the use of limestone or other source of calcium, and two-step synthesis with the use of calcium oxide (Gineika, Siauciunas et al. 2019). The problem is that most of the synthesized wollastonite products are in the hydrated form, and none of the products in the dry state has the crystal form of natural wollastonite (Andrews and Division 1970). Moreover, production of synthetic wollastonite is significantly more expensive than mining and processing of natural wollastonite, which hinders its market growth. According to report from industry analysts published by Lucintel in October 2018, natural wollastonite is forecasted to remain dominant type of product in the foreseeable future (Perry 2012).

Global wollastonite market is primarily affected by the changes in construction and infrastructure industries. Therefore, wollastonite industry is forecasted to grow every year and Asia Pacific (particularly China and India) is expected to remain the largest market for wollastonite due to growth in construction industry and market size of this region, which is eventually going to boost global wollastonite industry (Lopez 2019).

Diopside is another industrial mineral with composition $MgCaSi_2O_6$. It is a monoclinic pyroxene mineral, which is usually found in solid solutions with hedenbergite ($FeCaSi_2O_6$) and augite ($(Ca,Na)(Mg,Fe,Al,Ti)(Si,Al)_2O_6$) in ultramafic igneous rocks.

It has several potential economic uses, as a gemstone in two forms – black star diopside and chrome diopside, and as a performance additive in ceramics and glass industries, biomaterials, nuclear waste immobilization and fuel cell technology (Alekseev, Abakumov et al. 1995).

Diopside has good chemical and mechanical stability, high crystallization ability, bioactivity, as well as high bending and compressive strength capabilities. Moreover, the source of raw diopside is abundant and cheap, which makes it a potentially valuable additive in various applications (Almuhamadi, Karpukhina et al. 2014, Si and Li 2020).

Natural diopside is seldom discovered in deposits that simultaneously have a size, quality and location which allows economic development of the deposit. Nonetheless, there is some limited gem-quality diopside mining activity in Siberia, Russia, which is the main source of chrome diopside used in jewelry today. Diopside deposits found in many countries such as Austria, Brazil, Burma, Canada, Finland, India, Italy, Madagascar, Pakistan, South Africa, Sri Lanka, and the United States (King 2014).

1. Industrial Minerals

In general terms, industrial minerals are commercially valuable geological materials (rocks, minerals etc.) which are obtained by mining and does not belong to metallic or fuel type of raw materials. Comparing to metal or fuel type raw materials, industrial minerals are primarily valued because of their physical and chemical properties and, it is important to note that many industrial minerals require few or no prior processing at all and are used in their natural state in a wide range of applications (e.g., sand, gravel) (Ciullo 1996).

Industrial minerals contain a broad variety of minerals, from low value materials such as sand and gravel through to high value commodities like industrial diamonds. However, there is some substantial overlap between the four types of commodities: fuel, metal ore, industrial mineral and gemstone as some minerals can be used within an array of various applications. For example, some metal ores are also utilized as industrial minerals as described below:

- rutile (TiO_2) - titanium mineral and source of industrial titanium oxide pigments and other chemicals

- chromite ($FeCrZO_4$) - chromium mineral and raw material for the manufacture of chromium oxide-based refractories

- bauxite - rock comprised of hydrated aluminium oxides, utilized as aluminium ore and raw material for the refractories industry.

Additionally, it is quite common for industrial minerals to be derived as a by-product from an operation in which other major commodities are produced (e.g. Tyrnyauz Tungsten Mine in Russia, which also possess substantial reserves of wollastonite).

Moreover, there is a significant variation in the cost or market value of a particular industrial mineral, which depends on suitability of the mineral for a specific application. Aggregates like sand and gravel can be marketed directly from the quarry only for slightly higher than the cost of excavation, making the location of deposit and logistics an essential economic factor. For example, industrial minerals which need treatment by firing require higher prices due to energy costs and the greater capital expenditure of investing in processing plant and machines. Correspondingly, other materials which may require reasonable refining processes to reach particular technical specifications will command higher market price (Ciullo 1996).

Overall, there are eighteen of the most commonly used industrial minerals and eight major consuming industries, which are paints & coatings, papermaking, rubber, adhesives & sealants, plastics, ceramics & glass, pharmaceuticals, and agriculture (Manning 1995).

Wollastonite is one of the main silicate industrial minerals, as well as quartz, feldspar, talc etc., which are used in a wide variety of industries (Ciullo 1996). Generally, silicate minerals are defined as rock-forming minerals which consist of silicate groups, in other words, any mineral which has silicate and oxygen in its core structure is a silicate mineral. Hence, silicates minerals are one of the most common minerals on Earth making up approximately 90% of Earth's crust (Deer, Howie et al. 2013). However, most silicate minerals do not possess commercial value and those few which possess are called industrial.

1.2 Industrial Importance of Wollastonite

Wollastonite is often called versatile mineral, primarily because of its wide range of special properties such as high brightness and whiteness, low moisture and oil absorption, low volatile content, and acicular properties, which makes it valuable raw material in many applications. The largest application is ceramics, which takes around 40-45% of the total Wollastonite production (Lopez 2019). In ceramics, the primary application of wollastonite is manufacturing of tiles, where it is used because of features like low shrinkage, low warpage, strength and permeability for fast firing with minimum gas evolution (Deer, Howie et al. 2013).

Wollastonite is also used in plastic & rubber manufacturing industries, where it helps to increase durability of the composites utilizing properties like high acicularity and low oil and moisture absorption of the mineral. It is used in paints production due to its low oil absorption, high brightness, and whiteness properties (Deer, Howie et al. 2013).

Moreover, one of the most important applications of wollastonite is substitution of asbestos in fire-proofing applications. Asbestos is prohibited by many countries in the world because of its known adverse effects on health, while wollastonite proved to have no adverse effects on people's health and better fire-resisting properties comparing to asbestos. It is usually used in high temperature insulation boards, fire-resistant roofing tile, wallboard etc. (Ciullo 1996).

Also, wollastonite is used in metallurgy as a flux for welding, source of calcium oxide, a slag conditioner and as a protection for surface of the molten metal during the continuous casting of steel (Virta 2001). Finally, it used in coatings, production of glass etc., where it is primarily used as a reinforcing additive (Ciullo 1996).

Wollastonite has been used industrially only since the beginning of 20th century (first production started in 1935 in California, USA), and many of its properties are still investigated (Bulatovic 2015). For example, some of the recent promising studies showed that wollastonite can be effectively used in environmental remediation purposes (soil & water remediation) and as a crop fertilizer in agriculture (Van Bockhaven, De Vleesschauwer et al. 2013, Haque, Santos et al. 2019, Taylor, Driscoll et al. 2021). However, it is important to note that industrial mineral consumers are usually conservative by nature, and do not readily accept new products as noted by Harvey and Lagaly (2013). Often, it takes long time to convince and prove to the market and purchasing agents that the new product is compatible with their requirements and formulations, and that the product quality and supply are going to be consistent (Harvey and Lagaly 2013).

One of the extensive studies, which showed the advantages of using wollastonite as a reinforcing agent was conducted by Low and Beaudoin (1992). The study of the effects of wollastonite fiber addition to cement was conducted with the results showing significant improvements in the properties indicated below (Low and Beaudoin 1992):

Flexural Strength: Enhancement in flexural strength can be achieved by integrating an optimum amount of natural wollastonite micro-fibers and silica fume in the cement composite mixture. For example, a maximum flexural strength of more than 28 MPa (4080 psi) is achieved when a composite mixture consisting of 11.5% by volume of wollastonite micro-fibers and 5.2% silica fume is prepared with a water/cement and silica fume ratio of 0.35.

Ductility: Improvement of the pre-peak and the post-peak load- deflection response by the integration of wollastonite micro-fibers is attained in composite mixtures both with and without the presence of silica fume.

Microstructural Modification: The microstructure of cement-based composite systems is substantially enhanced by the integration of wollastonite micro-fibers and silica fume. The inclusion of wollastonite micro-fibers and silica fume develop pore discontinuity in cement-based systems, which, in turn, improve durability of the products.

Water Permeability: Adding wollastonite micro-fibers promotes lower water permeability, which is more efficient than when it is attained with pure cement paste, or with binders that have steel or carbon micro-fibers systems.

Chemical Stability: Wollastonite micro-fibers possess high chemically stability properties in hydrated cement and cement-silica fume composite matrices. The fibers are not affected by exposure to long-lasting hydration in calcium hydroxide solution.

As to the content requirements, wollastonite concentrates with a grade of at least 72% can be used in the production of porcelain glaze, which is distinguished by good gloss, even pouring and a small number of pricks. Concentrates containing at least 90% wollastonite and not more than 0.1% of impurity dyes and having a whiteness of at least 90% are used in the manufacture of any product where its addition have a positive effect (Marchevskaya, Tereshchenko et al. 2017)

1.3 Industrial Importance of Diopside

Diopside is used less in the industry comparing to wollastonite, however, there is a growing interest towards diopside as a cheap performance additive in the fields like ceramics, glass ceramics, biomaterials, nuclear and fuel cell technologies and dentistry.

Since 1970, blast furnace slags, which contained diopside and wollastonite, have been used to manufacture inexpensive type of glass ceramics called slagsitall. Its main advantages include high hardness, high wear and corrosion resistance, relatively low melting point, and low cost of production (Alekseev, Abakumov et al. 1995, Pinckney 2001). Since that time, Slagsitall has been widely used in the construction, chemical and petrochemical industries, where it is used to manufacture abrasion and chemical resistant floor and wall tiles, machine parts, chimneys, plungers, grinding media etc. (Pinckney 2001).

Many recent researches have brough to the attention the importance of diopside and its potential application in biomaterials and dentistry. Diopside is a bioactive material with high bending (300 Mpa) and compressive strength (1861 Mpa) which is stronger than human cortical bone (Almuhamadi, Karpukhina et al. 2014). Moreover, diopside does not have general toxicity in cell cultures, form a uniform junction with newly grown in vivo bones, supports bones regeneration and has lower degradation rate compared to bioglass and $CaSiO_3$ (Correlo, Oliveira et al. 2011). Due to these advantages, diopside has been recently claimed to be superior to other silicate bioceramic materials, including wollastonite (Baino, Tulyaganov et al. 2022).

2. Gravity and Magnetic Separation

2.1 Gravity Separation

Gravity separation is the method of separating minerals using their relative differences in densities. The methods of gravity separation have been used since long time ago. Moreover, the very first examples of gravity separation have been done by natural forces, when the Earth had significant changes in temperatures, creating expansions and compressions of matter, following by weathering and hydraulic fracturing which promoted liberation of native metals and valuable minerals. Finally, washout and transfer of minerals by water flows completed natural ore preparation – minerals with high densities precipitated quicker than minerals with low densities creating concentrated placers in lowlands of relief. The results of such natural processes can be seen on mines like Hill End in Australia, where some areas of the deposit contained up to 550 kg/t of gold (Verkhoturov 2006).

In fact, archeological excavations evidence that people started using gold around 6000 years ago. It is obvious, that the first method was a hand cobbing, which was then substituted by panning (Verkhoturov 2006).

Panning is considered as the oldest gravity separation method, which is followed by concentration on static and later shaking tables. The first shaking table was created by Arthur R. Wilfley in 1896. After some time, it was noticed that granular materials can be efficiently separated on the sieving pan, which is periodically submerged into water. The process was completely manual and was named as sieve jigging. The process was widely used by various mines and was later mechanized, which played a significant role in mineral processing development. The first piston jigging machine was used in Harz (Germany) in 19th century for lead processing. Then, in 1892 F. Baum invented first pistonless pneumatic jigging machine, in which pulses of water are generated by compressed air. Later, in 1920s heavy medium separation was first utilized for coal processing in the USA (Lopatin and Shokhin 1993).

The industrial use of gravity separation techniques has declined in the first half of the twentieth century due to the discovery of froth of flotation, an efficient way to separate minerals based upon their surface properties, which provided the mining industry an ability to selectively process low-grade complex ores. However, gravity separation remains as the primary concentrating process for iron and tungsten ores and is used widely for treating tin ores, coal, gold, beach sands, and many industrial minerals (Wills and Finch 2015).

Gravity beneficiation methods separate minerals of different specific gravity by their relative movement in response to gravity and one or more other forces, for example, resistance to motion created by a fluid like water or air. It is important to have a marked difference in densities between the mineral and the gangue to have an efficient separation. Moreover, it is essential to note that modern gravity separation methods do not rely solely on density properties and in many cases, shape and size of minerals also play substantial role (Verkhoturov 2006).

It is necessary for effective separation to have a marked difference in density between the mineral and the gangue. Approximate separation efficiency estimation can be obtained from the concentration criterion, $\Delta\rho$ (Eq 1).

$$\Delta\rho = \frac{\rho_h - \rho_f}{\rho_l - \rho_f} \tag{2.1.1}$$

Overall, if the concentration criterion between valuable and gangue mineral or minerals is above 2.5, then gravity beneficiation is considered relatively easy, if it is lower, then efficiency of separation decreases correspondingly with the concentration criterion. If it is lower than 1.25, it is either very difficult or not possible at all (Wills and Finch 2015).

Table 1. Efficiency Estimation based on Concentration Criterion for Gravity Separators (Wills and Finch 2015).

Concentration Criterion	Separation?	Useful for?
2.5	Relatively Easy	To 75 µm
1.75-2.5	Possible	To 150 µm
1.5-1.75	Difficult	To 1.7 mm
1.25-1.5	Very Difficult	
<1.25	Not Possible	

Gravity concentration methods are the primary methods for processing of anthracites and coal, it is widely used for processing of iron, manganese, tungsten, tin, gold, some rare earth ores and other minerals.

The main advantages of gravity separation are low cost of capital and operational expenditures and small environmental footprint comparing to other separation methods. Depending on deposit and ore characteristics, it can be more efficient and productive than other separation methods (Verkhoturov 2006).

There are many types of gravity separation used in the industry, below the most common of them are briefly described.

Conventional, in line pressure and centrifugal jigs

Basically, separation of minerals of differing densities is conducted in a bed resting on a ragging screen (Figure 2). Pulsating motion of diaphragm and an incoming flow of hutch water fluidizes the resting bed which is mixed with a bed of intermediate density particles. The heavier particles (high density and/or size) sink through the ragging due to pulsating and dilating motion of the bed and form an underflow concentrate and the lighter and smaller particles form tailing overflow (Ambrós 2020).

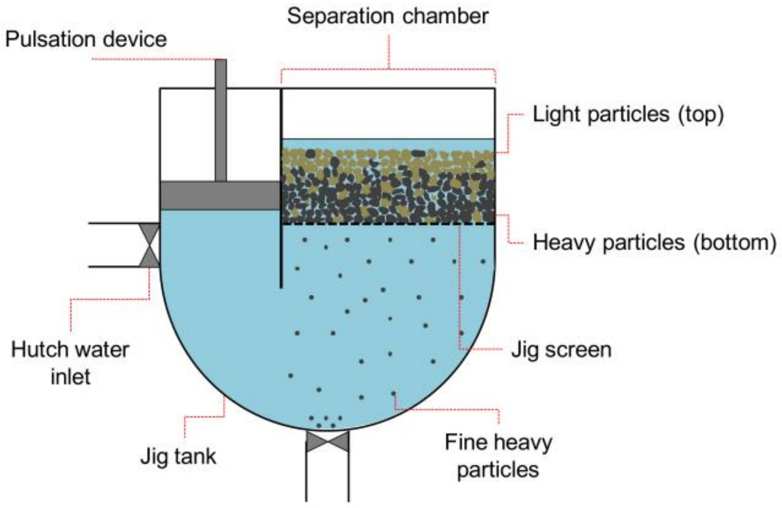


Figure 2. Basic representation of jig construction (Ambrós 2020).

Dense medium separators

Dense medium separation (DMS) is relatively modern gravity separation method which grew in popularity during the 1950-1970's as many companies utilized it to replace inefficient jigging processes for separating coal, iron and other ores. Basically, in this process, particles with a broad range of densities are introduced into a suspended medium of a given density (Figure 3). Particles that are lighter than the medium density float and particles that are heavier than the medium density sink (Gupta and Yan 2016).

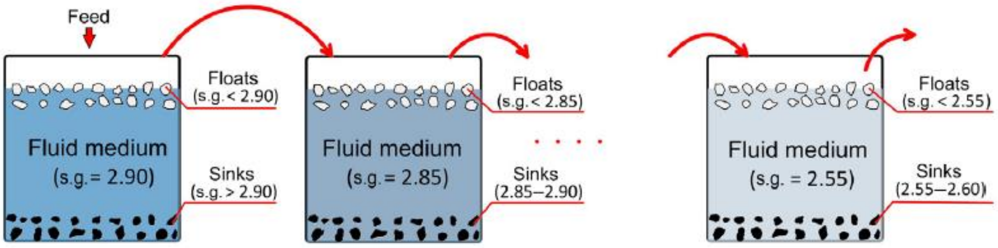


Figure 3. Representation of laboratory heavy liquid testing (Wills and Finch 2015).

Wash water and wash waterless spirals

The spiral is principally an inclined chute with a complex cross section wrapped around a central column (Figure 4). Separation is achieved by the combination of gravitational and centrifugal forces affecting particles of different densities – heavy particles follow the shorter route on the spiral, while lighter particles follow the longer trajectory on the spiral. The combination of these forces is greater than in the cone and, together with the lower slurry density usually used, produce a greater concentration ratio than the conventional pinched sluice and a higher recovery of fines (Andrew 2003).

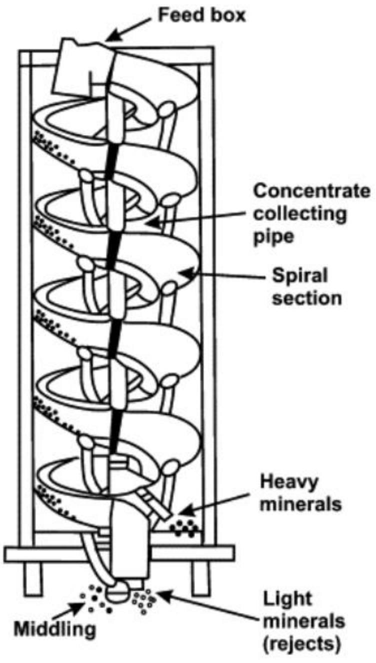


Figure 4. Typical representation of spiral classifier (Haldar 2018)

Wet shaking tables

The principle of separation is the movement of particles based on their SG and size moving in a slurry (in the case of wet tables) over an inclined table (Figure 5), which oscillates backwards and forwards essentially at right angles to the slope, in combination with riffles which retain the nearest to the deck particles. This motion and configuration leads to the fine high SG particles migrating nearest to the deck and carrying along by the riffles to discharge over the upper edge of the table, while the low SG coarser particles move or remain closer to the surface of the slurry and move over the riffles, discharging over the lowest edge of the table.

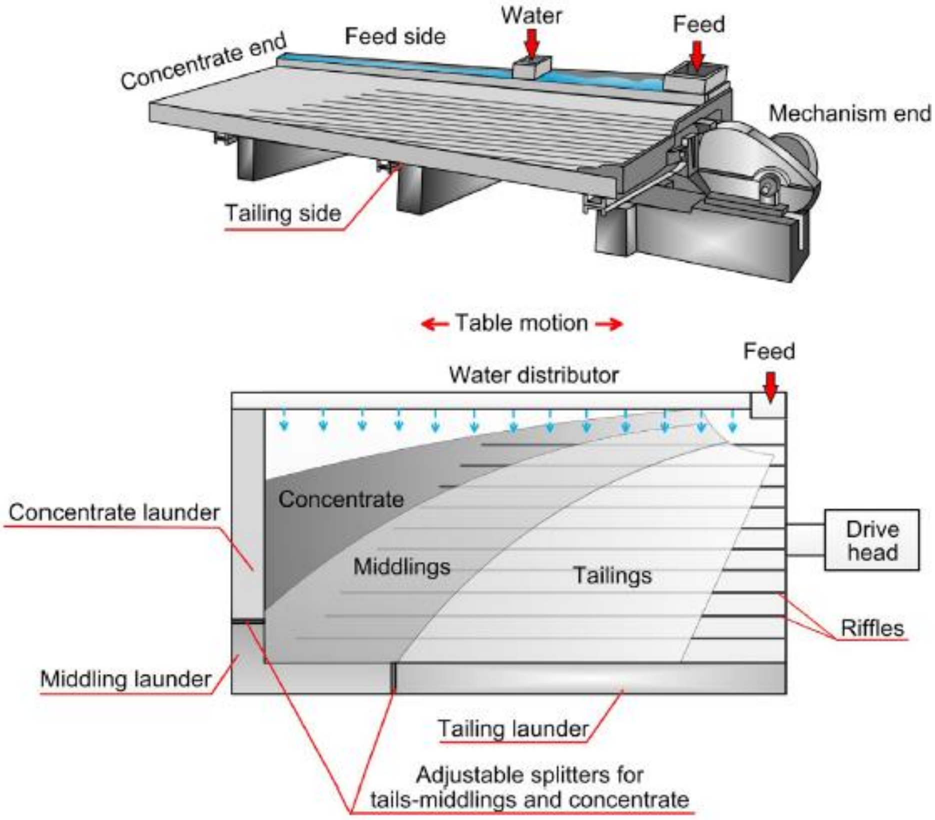


Figure 5. Wet shaking table (Wills and Finch 2015).

Falcon concentrators

Feed slurry is injected through a fixed feed tube into the concentrate cone (Figure 6). When the slurry arrives at the bottom of the cone it is forced outward and up the cone wall due to the effect of centrifugal force. Fluidization water is injected into the concentrate cone through a range of fluidization holes. The slurry fills each ring of the concentrate cone and create a concentrating bed, while the fluidization water prevents the compaction of the bed. The injected flow of water inside the rings is manipulated to maintain optimum bed fluidization. Particles with high specific gravities are captured and retained in the rings of concentrating cone. The high SG material can also replace low SG material that was previously in the riffles by the pressure created by fluidization water injected into the rings. Finally, when the concentrating cycle is complete, concentrates are flushed from the cone inside the concentrate launder (Wills and Finch 2015).

Multi Gravity Separator (MGS)

The MGS combines the centrifugal motion of an angled rotating drum (though the speed is lower) of a Kelsey jig or Falcon Concentrator, with the oscillating motion of a shaking table, to create an enhanced gravity separation, which is particularly suitable for fine particles processing (Figure 7).

The fundamental principle of MGS is based on centrifugal and oscillating motions forces that affect particles in a slurry flow distributed inside the rotating drum. Scrapers and wash water promote the high-density particles to move up the drum to discharge over the top lip, while the low-density particles flow in the opposite direction and discharge over the drum's lower lip (Andrew 2003).

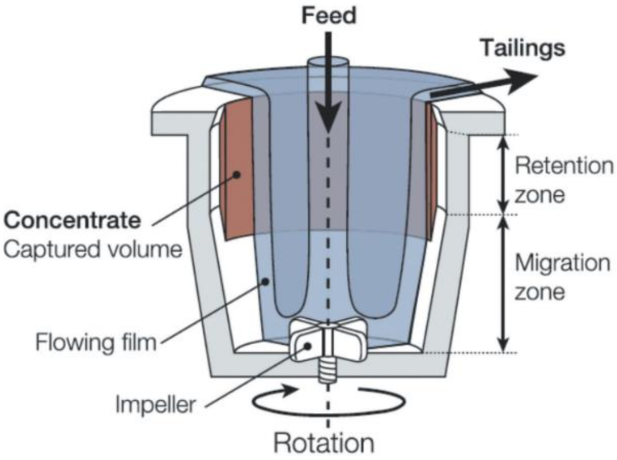


Figure 6. Schematic illustration of typical Falcon concentrator (Aksoğan Korkmaz 2021).

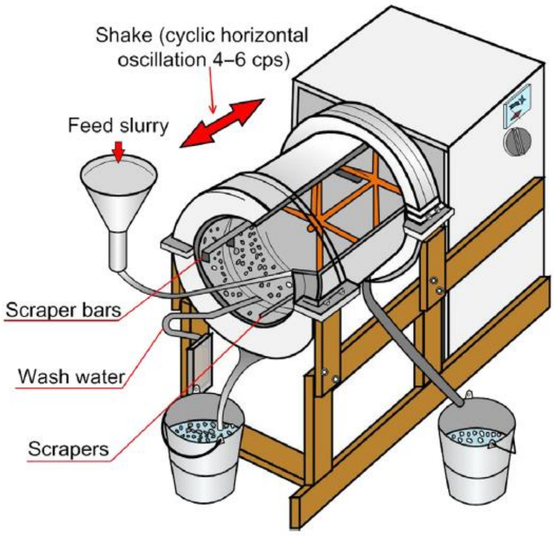


Figure 7. Pilot scale Multi Gravity Separator (MGS) (Wills and Finch 2015).

2.2 Magnetic Separation

For the first time, the phenomenon of magnetism was discovered by the Chinese, who used the polarity of the magnet and created a compass even before our era. First discovered attempts of using hand-held permanent magnets to remove magnetite from tin and other rare metal concentrates are dated back to XVII-XVIII centuries. However, the beginning of the industrial application of the magnetic method dates to the end of the 19th century, when in the USA - by Ball and Norton - and in Sweden - by Venstrom - the first drum separators with an electromagnetic system for the dry beneficiation of magnetite ores were developed (Pelevin 2015).

At the beginning of the XX century magnetic beneficiation of magnetite ores has received a relatively large development in Sweden, which was associated with the development in 1906 by Grendal of the first drum separator for wet separation. The creation of this separator, which is the prototype of modern drum separators, made it possible to successfully and economically enrich fine grades of magnetite ores (Karmazin 2005, Pelevin 2015).

At the end of the XIX century, in order to process weakly magnetic ores, Veterill (USA) developed a belt separator with a closed electromagnetic system and pointed poles, in which an increased magnetic force was achieved. Subsequently, disc, roll and roller separators, as well as high-gradient separators, were developed in different parts of the world for processing of weakly magnetic ores (Pelevin 2015).

Principally, magnetic beneficiation is based on the difference in the magnetic properties of the separated minerals. Magnetic properties include magnetic susceptibility and magnetic permeability. Magnetic permeability shows how many times the magnetic field in a substance is greater than in vacuum. Magnetic susceptibility determines the behavior of particles in a constant magnetic field and expresses the ability of bodies to be magnetized.

A magnetic field is a space in which the action of magnetic forces on magnetized bodies is performed. Magnetic fields can be uniform or non-uniform. Uniform fields are observed with flat and parallel surfaces of the magnet poles, non-uniform - with pointed poles. In a homogeneous field, the intensity at any point is the same, in an inhomogeneous field, it increases or decreases gradually in one direction. It is important to note that magnetic separation occurs only in a non-uniform magnetic field (Karmazin 2005).

According to magnetic properties minerals are divided into:

• Strongly magnetic minerals – e.g., magnetite, pyrrhotite.

• Weakly magnetic – e.g., wolframite, garnet, ilmenite.

• Non-magnetic – e.g., quartz, calcite, apatite.

Principally, all materials are affected in some way when placed in a magnetic field, although with many substances the effect is too small to be easily detected, so they are usually considered non-magnetic. According to that, all materials can be classified into two wide groups, according to whether they are attracted or repelled by a magnet (Wills and Finch 2015):

1. Diamagnetic substances are repelled along the lines of magnetic force to a point at which the field intensity is smaller. The forces acting here are very small, so the diamagnetic materials are usually referred to as “nonmagnetic”, even though this is not strictly correct. In the process of magnetic separation diamagnetic minerals are reported to the nonmagnetic product due to their inability to be affected by magnetic attractive force.

2. Paramagnetic materials are attracted along the lines of magnetic force to points of greater field intensity. Paramagnetic materials are reported to the "magnetic” product during magnetic separation as they experience attractive magnetic forces.

Magnetic beneficiation methods are usually used for (Pelevin 2015):

- Beneficiation of ferrous ore, as well as iron, manganese ores and minerals of alluvial deposits.
- Removal of ferruginous impurities from non-metallic minerals, e.g., glass, ceramic, abrasive and other raw materials.
- Regeneration of heavy medium suspensions (extraction of magnetite and ferrosilicon);
- Removal of random iron objects from various products of concentrating plants (crusher feed, concentrates produced by dry processing, etc.).
- Processing of sludge and tailings of beneficiation plants; slags of metallurgical production; cable, radio-electronic and other scrap of non-ferrous and ferrous metals; municipal solid waste.

Generally, magnetic separators are classified into low- and high-intensity separators and a high-gradient magnetic separators (HGMS). Also, low- and high-intensity separators are usually classified into dry and wet separators.

Wet Low-Intensity Magnetic Separators

Both wet and dry low-intensity separators are utilized to process ferromagnetic and some highly paramagnetic minerals. Principally, the separator consists of a drum with a six-pole magnetic system (Figure 8). Drum diameters is typically 900, 1200 or 1500 mm (Karmazin 2005). The outer surface of the drum is covered with rubber. The lower part of the drum is immersed in a bath made of non-magnetic alloys and having special holes for the non-magnetic fraction. Magnetic particles are attracted to the surface of the drum and carried through a special threshold into the discharge chute.

Dry Low-Intensity Magnetic Separators

Dry low-intensity magnetic separation is limited primarily to the concentration of coarse sands which are highly paramagnetic, a process known as “cobbing,” and is usually carried out using drum separators (Figure 8) (Wills and Finch 2015). These separators have two pairs of drums with a typical diameter of 630 mm, arranged in two tiers. The initial ore is fed from above and evenly distributed over two drums. After the first pair of drums, a magnetic concentrate and middlings are obtained, which enters the second pair of drums where the rest of tailings and middlings are produced.

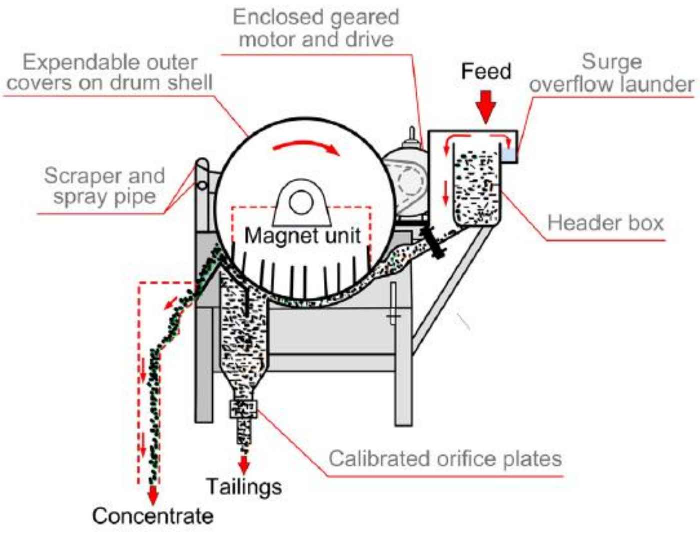


Figure 8. Representation of a typical drum magnetic separator (Wills and Finch 2015).

Wet High-Intensity Magnetic Separator (WHIMS)

High-intensity magnetic separators are designed to process weakly paramagnetic minerals. Development of continuous WHIMS is considered as the greatest advance in the history of magnetic separation (Shao, Veasey et al. 1996). Principally, it is usually a drum separator with feed from the bottom side. The material enters the feed hopper, from where it is directed to the working area of the separator. Magnetic particles are attracted to the teeth of the roll and carried out into the area of the weakened magnetic field where they are discharged.

Dry High-Intensity Magnetic Separator

Dry high-intensity separation is primarily confined to ores containing little, if any, particles finer than about 75 μm (Mohanraj, Rahman et al. 2021). The separator usually consists of four rolls. The two upper rolls are used for the main enrichment operation, and the two lower rolls are used for recleaning the non-magnetic fraction.

High Gradient Magnetic Separator (HGMS)

HGMS is primarily utilized for wet beneficiation of weakly magnetic materials. These separators differ from drum separators by the presence of small carrier magnets in their working space. Small balls and other small iron materials are used within this process. The separator consists of a drum, inside of which a five-pole magnetic system is fixed (Figure 9). The working space is filled with steel balls. The raw material from the feeder in the form of pulp is fed to a layer of balls, which is held on the drum by the field of the magnetic system. Non-magnetic particles are filtered through a layer of balls and enter the tail section. The magnetic particles rise together with the balls to the upper part of the drum and fall on the sieve, where the magnetic particles are washed with water (Ge, Encinas et al. 2017).

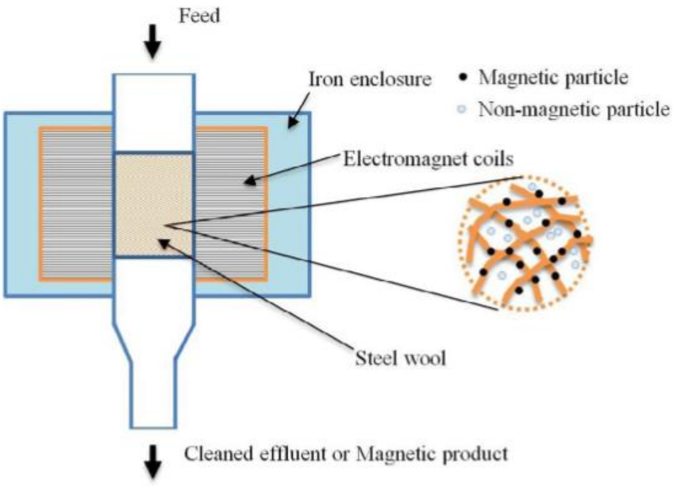


Figure 9. Schematic representation of HGMS process (Ge, Encinas et al. 2017).

There are many parameters which affect the process of magnetic separation and the primary of them are described below (Pelevin 2015).

1. Magnetic field strength. An increase in the magnetic field strength leads to an increase in the magnetic force, and as a result, it makes it possible to extract minerals with a lower magnetic susceptibility into the magnetic fraction. This affects the yield and quality of the separation products. But an excessive increase in the magnetic field strength can lead to increased clogging of the magnetic fraction. Insufficient field strength is the cause of the loss of magnetic minerals.

2. Working area parameters. With an increase in the diameter of the drum, the length of the working zone increases, and this makes it possible to increase the extraction of the magnetic fraction. Increased productivity is achieved by increasing the length of the drum.

3. Speed of rotation of the drum and rolls. It determines its productivity and quality of enrichment products. The rotation speed is selected depending on the enrichment method (dry or wet), feeding method (top or bottom), magnetic susceptibility and fineness of the separated minerals.

4. The size of the material. With a sharp difference in the size of minerals, it is difficult to choose the strength of the magnetic field, the parameters of the working zone, and the performance of the separator. All this leads to a deterioration in the technological parameters of enrichment. The best performance is obtained using a preliminary classification of the material.

5. Power density. With an increase in the solid content in the pulp during wet magnetic separation, the productivity of the separator increases, but the quality of the enrichment products decreases.

3. Flotation

Flotation is considered the most important and versatile mineral separation technique, which is still expanding its area of application and use. Originally developed to treat sulfide minerals containing copper, lead and zinc, it has expanded to beneficiation of nickel, platinum, and gold hosting sulfide ores, oxide minerals such as hematite and cassiterite, nonmetallic minerals such as fluorite, talc, phosphates, potash etc., fuel minerals, fine coal, and bitumen (Wills and Finch 2015, Gupta and Yan 2016). Moreover, flotation is even used in recycling and for the treatment of various types of wastewater, which is one of the actively developing fields of environmental technology nowadays. For example, it is possible to remove ink from recycled paper to produce new paper; the Kodak Company utilize froth flotation to separate metallic silver from photographic residues. Colloidal suspensions, bacteria, and traces of harmful metallic ions are removed by a modified flotation process - ion flotation or precipitate flotation (Wang 2010).

Historically, flotation has found prominence because of the need to process complex or low-grade ores where gravity separation techniques could not be applied due to fine particle size of the ore or insufficient difference in mineral densities. In a basic sense, flotation relies on the differences in surface properties of minerals, the property, which has never been utilized in mineral processing before the 20th century (Gupta and Yan 2016).

3.1 Flotation Principles

Flotation is a separation technique which is based on the natural (and induced) differences in surface properties of minerals. Minerals with *hydrophobic* surface property are those, which repel water and tend to attach to air bubbles, while minerals with *hydrophilic* surface property are easily wetted and do not attach to air bubbles (Figure 10). Hence, hydrophobic minerals are floated and collected in the froth, while hydrophilic minerals stay in the liquid phase. Overall, the system is complex, involving three phases (solids, water, and air) and the interaction of chemical and physical variables. Chemical variables are those, which control the surface chemistry and its transition between hydrophobic and hydrophilic states. Ore properties like size distribution and liberation, parameters of flotation cell, air rate and bubble size are physical variables. Therefore, because of complex interaction of chemical and physical variables, flotation is often defined as *physicochemical* based process (Wills and Finch 2015).

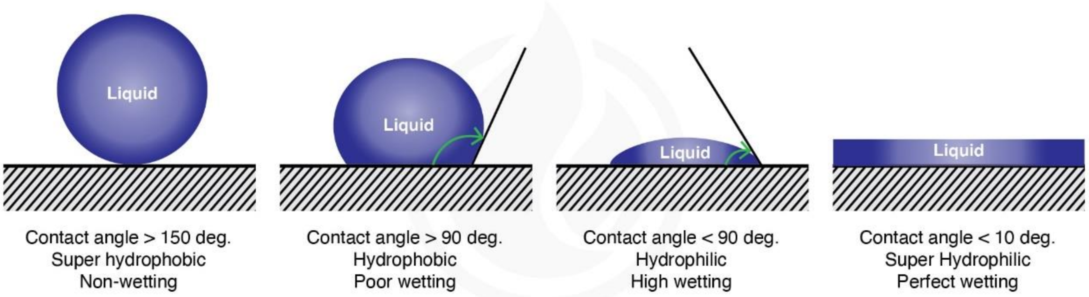


Figure 10. Illustration of hydrophobic and hydrophilic surface properties and their contact angles (Wang 2010).

Froth flotation process differs from other separation processes by the ability to change and control the respective interfacial tensions and surface charges of treated materials. The ability to change the relative properties of different interfaces in the system makes the flotation process more versatile and universal comparing to other separation processes, which utilize invariable physical properties like specific gravity, magnetic separation etc. (Rao 2004).

Basic flotation machine representation can be seen on Figure 11, where air is introduced inside the cell through an agitating shaft of an impeller, which, in turn, agitates the pulp and helps to generate relatively small air bubbles. As a result, hydrophobic minerals get attached to air bubbles, rise to froth, and get collected in the concentrate launder, while hydrophilic mineral particles stay in the pulp phase and then exit the cell as tailings (Wills and Finch 2015).

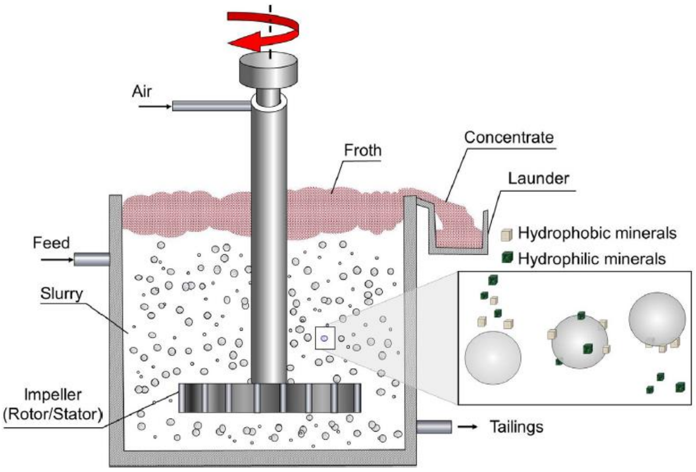


Figure 11. Basic representation of a flotation machine (Wills and Finch 2015).

In flotation, valuable minerals are usually collected in the froth fraction, while gangue minerals stay in the pulp phase exiting flotation cell as tailings. This is called *direct flotation*, and the opposite configuration, where gangue minerals are collected in the froth phase and valuable minerals are left in the pulp zone, is called *reverse flotation* (Gupta and Yan 2016).

The raw material mined from any deposit usually consists of highly heterogenous mixture of solidified phases, which are mostly crystalline and comprise of various minerals. Less often, the mined ore is none crystalline, for example, coal, glasses, resins etc. In addition, in most cases the valuable mineral content in those ores is low and needs to be freed up or liberated by undergoing size reduction processes in order to treat the ore in the subsequent process like flotation. Moreover, in most cases, degree of liberation is of utmost importance for the efficiency of flotation, considering that the main separation factor in the flotation process is a surface property of minerals, which should be physically open and not encapsulated within a rock to be able to utilize it. It should be noted, that the cost of grinding may account for a large portion (40-60%) of the total treatment costs involved in recovering the minerals from the ore (Rao 2004).

When grinding produce sufficient amounts of liberated valuable minerals, first of all, this ore in the form of slurry goes to rougher stage flotation, where rougher concentrate is produced. The remaining valuable minerals, which did not float in the rougher stage due to incomplete liberation, are then concentrated in further scavenger flotation stage. Unliberated minerals typically need longer flotation time and higher reagent dosages for their flotation.

For rougher concentrate, where valuable minerals have primarily high degree of liberation, cleaning and recleaning stages are conducted to achieve higher concentrate grade mainly through the removal of mechanically entrained gangue particles. The entrainment of hydrophilic gangue particles in the froth usually occurs due to disturbances created by mechanical mixing of the slurry within the flotation cell, the effect of which can be considerably decreased in column cells without impellers.

3.2 Flotation Reagents

When the hydrophobic mineral particles reach the surface of the pulp, the only force which can support the particles in this zone is a layer of stable froth. Moreover, natural degree of hydrophobicity of a mineral is usually not enough to conduct an efficient separation. Therefore, to achieve optimum flotation conditions, it is necessary to use numerous chemical compounds known as flotation reagents (Wills and Finch 2015, Gupta and Yan 2016).

The surface properties of different solids are usually regulated by various chemical agents. Overall, there are three types of flotation reagents used in flotation:

1. *Collectors*: organic chemicals which can change the hydrophobicity of the mineral surface and hence make the mineral capable of being collected in the process.
2. *Frothers*: organic chemicals which reduce the surface tension of the water to stabilize the bubbles into a froth layer at the top of pulp phase to collect and separate hydrophobic minerals.
3. *Modifiers*: organic or inorganic chemicals used to modify the pulp conditions to enhance the difference in surface chemistry between the valuable and gangue minerals.

Results of a flotation process are primarily affected by its reagent regime – assortment, dosages and the way of utilization of reagents; same flotation results can be achieved with various reagent regimes. Flotation reagent regime is mainly determined by the type and characteristics of the ore, particle size distribution and requirements for the flotation products (Ivankov and Shubov 1990).

The simplest reagent regime usually includes no more than one reagent (which possess collector and frother properties together) or one collector and one frother. Nowadays, simple reagent regimes are seldom. Usually, flotation process includes several reagents simultaneously, which are interconnected with each other in reaching the overall objective of the process (Ivankov and Shubov 1990).

The most important flotation reagents are the *collectors*, which generally absorbs on the surface of a target mineral, making it more hydrophobic to facilitate the strong bubble attachment (Figure 12). Collectors are basically heteropolar organics with a charged polar group and an uncharged non-polar group. The non-polar group is typically a hydrocarbon chain and in the early years of development of flotation process this hydrocarbon chain was in the form of oil. The oil based flotation was replaced in the early 1920's by the emergence of more selective organics such as the xanthates and dithiophosphates. Oil in the form of kerosene or diesel is still used as the primary collector in the coal and other industries (Gupta and Yan 2016).

Collectors may be non-ionic (hydrocarbon oils) or ionic. The ionic collectors are either cationic, (amines) or anionic (fatty acids or sulphydril compounds such as xanthates or dithiophosphates) (Gupta and Yan 2016).

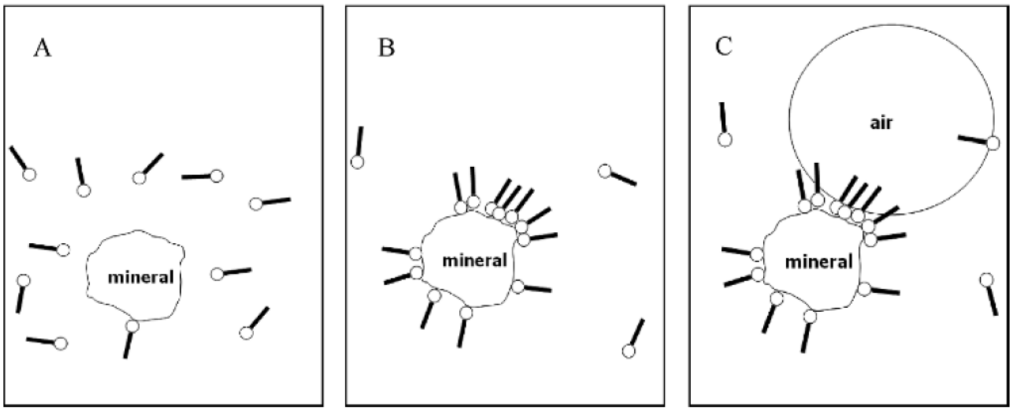


Figure 12. (A) Collector dissolved in the aqueous phase, (B) adsorption onto a mineral surface and (C) attachment of an air bubble onto the hydrophobic surface (Gupta and Yan 2016).

Frothers are surfactants, usually organic heteropolar compounds such as alcohols or polyglycol ethers, which are used to create and sustain stable froth phase on the surface of the pulp and produce smaller air bubbles, which are necessary to increase collision rates within the pulp phase. Because of the heteropolar nature, the frother adsorbs at the air/water interface and as a result, decreases the water surface tension. This has the effect of generating smaller bubbles and more importantly it stabilizes the froth when it reaches the top of the pulp. If the bubbles burst when they reach the air/water surface, then the minerals they carry will drop back into the slurry adversely affecting the recovery of valuable minerals. Hence, the main role of the frother is to stabilize the froth formed at the top of the slurry long enough for the concentrate to be removed from the flotation cell. However, once removed from the cell, the froth should break to allow the mineral particles to be treated by the further processing stages (Wills and Finch 2015, Gupta and Yan 2016).

Commonly used frothers are usually natural chemicals like pine oil, cresylic acid and synthetic reagents such as methyl isobutyl carbinol (MIBC) and polyglycol ethers. Ideally frothers should have little or no collecting properties and vice versa so that both functions can be controlled separately (Wills and Finch 2015).

The purpose of regulating or modifying agents is to prepare the surfaces of different solids for the following selective adsorption of the surfactant in a way that only the necessary particles are made hydrophobic. This surface regulation is achieved through pH control, establishment of an appropriate oxidation-reduction level in the system, and through control of ion concentration. In case of absence of appropriate modifying reagents, the adsorption of surfactant may be incomplete for the generation of hydrophobic surfaces of desired minerals, or the effect may be spread unselectively to both desired and undesired minerals decreasing overall selectivity of the process (Rao 2004).

Therefore, modifiers or regulators are basically required to control the flotation process by activating or depressing attachment of mineral to air bubbles, control particle dispersion and regulate pH of the system. Modifiers are usually divided into depressors, activators and pH regulators (Wills and Finch 2015).

A depressant is any chemical which inhibits the adsorption of a collector by a mineral particle and thereby prevents its flotation (Gupta and Yan 2016). An activator changes the surface of the mineral to enhance the adsorption of the collector. pH regulators adjust the pH of the slurry to give optimum performance for a particular ore or reagents regime. The common pH regulators are lime, soda ash and sulphuric acid. Other reagents that may be used in specific cases include dispersants for removing clay slimes from mineral surfaces precipitants for removing interfering ions from solution.

As it can be inferred now, the success of the froth flotation process depends substantially on the proper control of surfaces and interfaces present in the highly complex mixture of several solid phases suspended in liquid solution through which air bubbles are being dispersed. Therefore, an appropriate use of specific collectors, modifiers, and frothers will be able to provide effective separations of various solid phases. The effective operation of a complex flotation process is also substantially dependent on other variables which are not physicochemical or surface chemical in nature. The hydrodynamics of the flotation pulp in various cells, the technology of flotation circuits, and an optimum integration of procedures comprising the particular industrial operation significantly affect the overall result of the flotation process. Therefore, the technical efficiency and the economics of the process are determined by a combination of different parameters. However, the role of surface chemistry is, frequently, the crucial factor in the success or the failure of a given flotation process technology.

Sulfide minerals are usually recovered by thiocollectors such as xanthates. Non-sulfide ores of heavy metals (oxides, carbonates, and sulfates) are collected either by xanthates after some prior sulfidization or by carboxylates and sulfonates. Nonmetallic minerals (silicates and insoluble salts such as $BaSO_4$, calcium phosphates, etc.) are collected using alkyl amines, alkyl sulfates, or carboxylates. The readily soluble sodium and potassium salts are separated from each other by flotation in highly concentrated brine solutions using n-alkyl amines or fatty acids. Flotation processes separating sulfur, coal, or bitumen from tar sands is considered as another distinct group of systems utilizing mostly nonionized surfactants (Rao 2004).

3.3 Flotation of Silicate Minerals

Silicate minerals are very diverse and practically always found in mined ores, often in significant quantities. With the development of flotation beneficiation technology, an increasing number of silicate minerals are moving from the category of rock to the category of valuable industrial minerals (Abramov 2008).

Probably, the main difficulty in the selective flotation of silicates is the similarity of their flotation properties. Flotation selectivity is achieved by selective activation or depression of separated minerals as a result of acid or alkali treatment, loading of hydrofluoric and sulfuric acids, sodium fluoride and sodium fluorosilicate, water glass and other reagents. It is widely practiced using softened water, preliminary washing of ore to deslime the pulp before flotation, cleaning the surface by mixing in dense pulp and other methods that increase the selectivity of silicate flotation by anionic and cationic collectors (Abramov 2008).

To date, among silicate minerals, the flotation of feldspars, beryl and spodumene ores, aluminum-containing raw materials and some other types of ores are the most common. Both anionic and cationic collectors are utilized in the flotation of silicate minerals, with fluoride ion additions used as the strongest modifier.

Silicates are separated by selective flotation, first, with the objective of concentrating a given component, e.g., quartz for glass manufacture, feldspar for ceramic use, and spodumene for production of lithium. Another goal of selective silicate flotation may be to remove the unwanted contaminant, for example, sodium and potassium feldspars from quartz produced for Portland cement, or to remove mica, etc. The success of selective silicate separation depends heavily on the use and type of modifying agents, control of pH, and the choice of collectors of suitable structure (Rao 2004).

4. Beneficiation of Wollastonite

Although wollastonite has been commercially mined and processed for more than 70 years, there has been very little research done on the processing technology, especially flotation over those years. In practice, wollastonite is commonly beneficiated either by mechanical sorting, magnetic separation, reverse flotation or by combination of these techniques, depending on specific ore characteristics and requirements for the final concentrate (Kangal, Bulut et al. 2020).

4.1 Gravity and Magnetic Separation

Mechanical sorting is applicable for wollastonite ore being in the form of large crystals. Simple hand cobbing and sorting can be used to separate wollastonite from the host rock, which is then sold in lump form. One of the examples where simple manual separation methods are utilized is Belka Pahar mine located nearby Sirohi, Rajastan, India (Ravi, Krishna et al. 2014). Firstly, the run-of-mine is separated by manual sorting to remove the gangue minerals, such as, calcite, diopside, garnet, quartz, and iron, then, it is crushed to various sizes to meet requirements of specific wollastonite consumers.

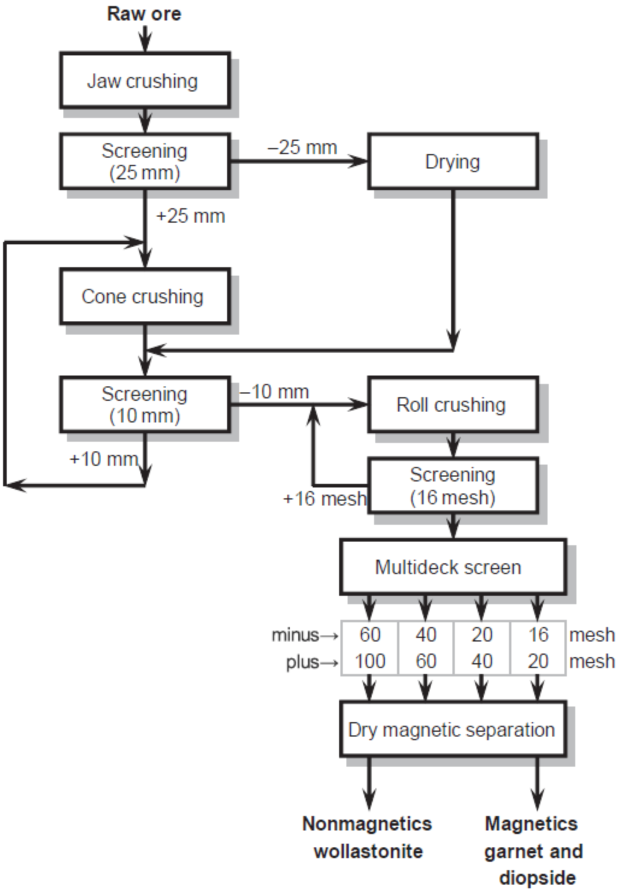


Figure 13. General flow sheet used for recovery of wollastonite using dry magnetic separation (Bulatovic 2015).

Minerals like diopside and garnet are usually removed using magnetic separation methods, whereas quartz and calcite by flotation. Typical flow sheet used for recovery of wollastonite using dry magnetic separation is presented in Figure 13. Wet magnetic separation proved to be highly efficient with ultrafine sizes – from 44 μm down to 1 μm, while dry magnetic separation is commonly used for sizes from 44 – 840 μm (Andrews and Division 1970).

4.2 Wollastonite Flotation

While mechanical sorting and magnetic separation alone are often not applicable to wollastonite processing due to relative inefficiency of the processes comparing to flotation, it is important to notice that wollastonite flotation tend to be challenging due to similarity of flotation properties of gangue minerals in wollastonite ores (Bulatovic 2015). In addition, needle-like shape of the mineral is also creating problems for an efficient separation of wollastonite from gangue minerals using flotation. Usually, reverse gangue flotation followed by separation of gangue minerals from wollastonite is utilized (Figure 14). For instance, wollastonite ores with calcite minerals are first floated to separate calcite using sulfate soap and followed by gangue flotation to remove minerals like silica or feldspar using amine flotation (Bulatovic 2015).

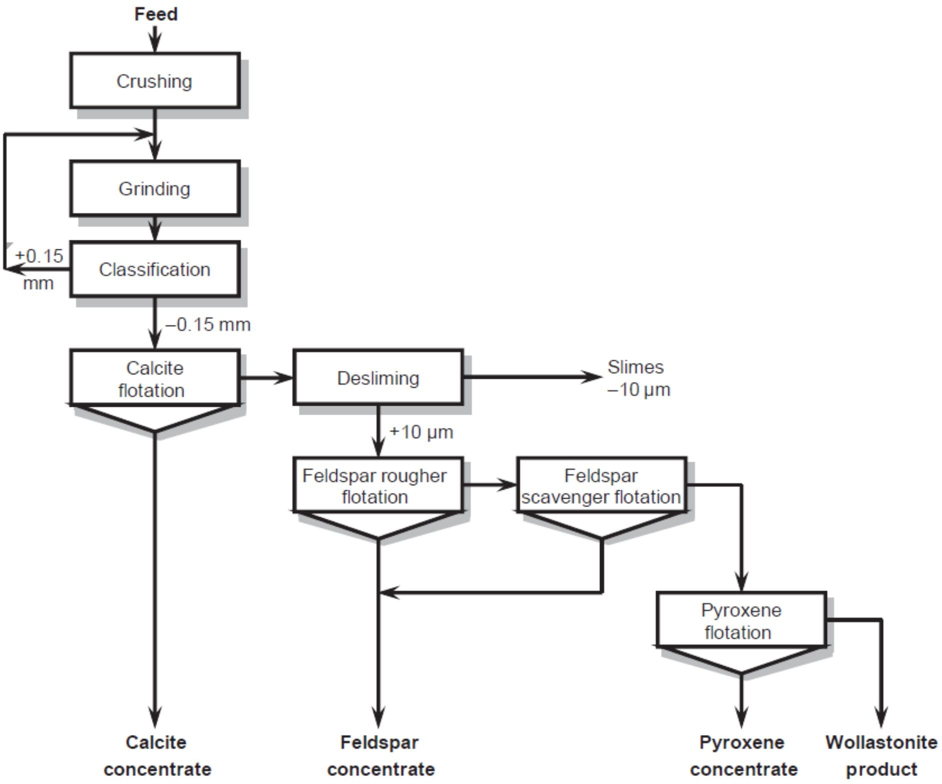


Figure 14. General flow sheet of reverse wollastonite flotation (Bulatovic 2015).

The commonly associated minerals in the wollastonite ore are:

Diopside = CaMgSiO6

Tremolite = $Ca(MgFe)_5Si_8O_{22}(OH_2)$
Idocrase = $Ca_{10}Al_4(MgFe)_2(Si_2O_7)(SiO_4)_5(OH)_4$
Grossulat Garnet = $Ca_3Al_2(SiO_4)_3$ and
Andradite Garnet = $Ca_3Fe(SiO_4)_3$

Koitash deposit in Uzbekistan contains around 50% wollastonite, 25% calcite and smaller proportion of minerals like feldspar, diopside, quartz, pyroxene, mica, etc. (Sadullayev, Asilov et al. 2021). Firstly, pyroxene and other magnetic minerals are separated by magnetic separation. After that, non-magnetic fraction is undergoing calcite flotation, where such reagents as sodium hydroxide, sodium silicate, sulfate soap and pine oil are added. Then, tailings of calcite flotation are undergoing quartz and feldspar flotation, where complex amines are used as a collector. Finally, high grade wollastonite is produced in the form of tailings of quartz and feldspar flotation.

In Russia, Tyrnyauz deposit with 15% wollastonite content was studied by Kola Mining Institute of Russian Academy of Science to find an efficient beneficiation method, which could increase the final concentrate grade above 65% (Marchevskaya, Tereshchenko et al. 2017). Tyrnyauz deposit is primarily utilized to mine wolfram and molybdenum ore, however, the deposit has also some reserves of wollastonite, which can potentially be mined and processed as a by-product.

First, X-ray sorting was identified as an efficient preconcentration stage to treat -50 +20 size fraction, which can increase wollastonite feed grade 1.5 times. In addition, the loss of wollastonite in this stage was below 9%. After X-ray sorting, magnetic separation with 30 A/m magnetic strength was used to separate pyroxene, garnet and vesuvian with the stage recovery of 92-98%.

Reverse flotation was conducted to float calcite from non-magnetic product of magnetic separation in order to get wollastonite concentrate as a sink (Figure 16). Distilled tall oil soap was used as a collector with the dosage of 300 g/t and Na_2SiO_3 as a wollastonite depressor with 100 g/t dosage rate, pH was between 8-9. After three stages of flotation, final wollastonite concentrate grade was 86.4% and the overall recovery was 52.3% (three stage flotation recovery was 74.9%). At the same time, overall wollastonite recovery without X-ray preconcentration stage was 32.4%, which is significantly lower than the overall recovery which includes X-ray preconcentration.

Swarna, Kota et al. (2003) investigated wollastonite interaction with an amine collector type. The study showed that at low pH values, the flotation performance worsens due to weak negative surface charge of wollastonite, while at higher pH, the wollastonite surface charge becomes more and more negatively charged leading to higher degree of attraction of diamine ions. It can be seen from Figure 16 that the optimum wollastonite flotation pH was determined in the range of 8.5-10.5. (Swarna, Kota et al. 2003).

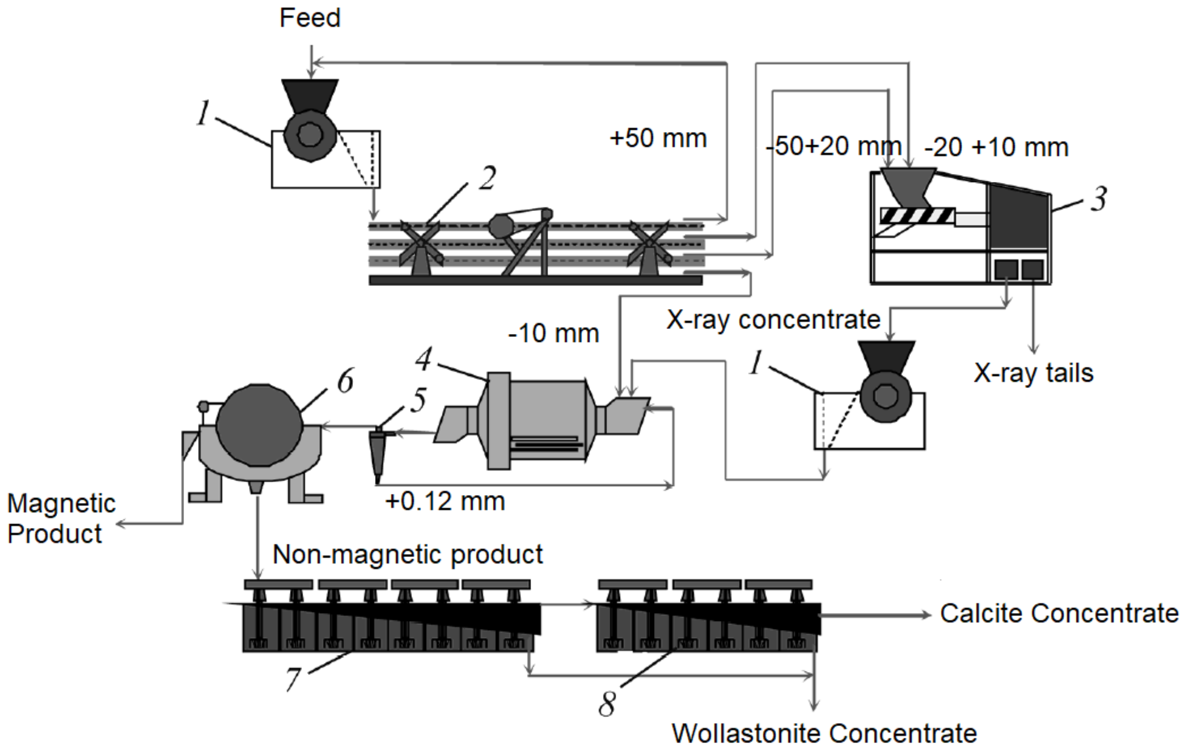


Figure 15. Proposed wollastonite beneficiation flow sheet for Tyrnyauz deposit (Russia) (Marchevskaya, Tereshchenko et al. 2017): 1 - jaw crusher; 2 - screening conveyor; 3 - X-ray separator; 4 - rod mill; 5 - hydrocyclone; 6 - magnetic separator; 7, 8 – reverse

Another study on wollastonite flotation was done by Çinku, Ipekoğlu et al. (1997). The study was conducted on Karakoy wollastonite deposit in Turkey, which contains 47.56% SiO_2, 39.86% CaO and 1.33% Fe_2O_3. The goal of the study was to produce wollastonite concentrate for ceramic industry, which has the following requirements for the concentrate quality - a minimum 49% SiO2 and 43–45% CaO, maximum 0.25–0.50% Fe2O3, and a maximum 1.5–4% loss on ignition. In the study, the initial ore was crushed and milled to 0.3 mm before undergoing magnetic separation. Boxmag type high intensity disc magnetic separator was used for the experiment with determined optimum parameters being 2 mm disk height, 17000 Gauss magnetic field strength, and 5 rev/min band rotation speed. The result of magnetic separation is decrease of Fe_2O_3 content from 1.33% to 0.24%. Then magnetic separation concentrate went to reverse flotation, where calcite was floated and wollastonite was depressed. Caustic soda was used as a pH modifier sodium silicate as a depressant and oleoylsarcosine and oleic acid were used as collectors. The resultant concentrate contained 57.10% SiO2, 40.88% CaO, 0.30% Fe2O3 and 0.13% loss on ignition. As a result of the flotation tests, 1000 g/t of collector, pH 10.5, 1.7 kg/t of sodium silicate, and 500 g/t of caustic soda were identified as the optimum flotation conditions. The concentrate quality requirement have not been fully satisfied due to slightly low content of CaO, therefore, further quartz flotation was recommended for this concentrate (Çinku, Ipekoğlu et al. 1997).

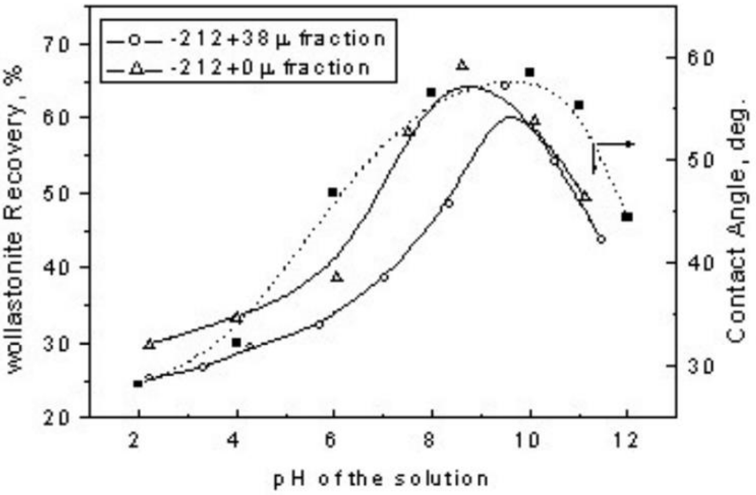


Figure 16. Relation of direct wollastonite recovery and pH of the solution (Swarna, Kota et al. 2003).

The Saint Lawrence wollastonite deposit in Ontario (Canada) has estimated reserves of 9 Mt at an approximate grade of 40-44% wollastonite (Grammatikopoulos, Clark et al. 2003). The wollastonite skarn is associated with the Grenvillian metamorphic region, which was presumably formed due to infiltration metasomatism of limestones by magmatose, silicarich, CO2-poor hydrothermal fluids. The main gangue minerals associated with wollastonite are diopside (31%), feldspar (17%), quartz (6%) and other minerals in smaller amount like calcite, pyrrhotite, pyrite, chalcopyrite, titanite and graphite.

As a result of several years of extensive studies, an optimum process has been developed for the beneficiation of this ore (Figure 17). The gangue minerals contained in the ore have similar flotation properties as wollastonite and therefore selective flotation of wollastonite from the gangue minerals is quite difficult. Another issue related to selective flotation of wollastonite is the shape of wollastonite crystals. Wollastonite crystals are needle-like at an aspect ratio above 8, so attachment of wollastonite on the air bubbles is inefficient. As a result of that, reverse flotation method was chosen as the optimum flotation configuration (Bulatovic 2015).

Excellent wollastonite depression during gangue flotation was achieved using acetic acid. Other important parameters such type of collector, pH and flotation configuration were optimized as well. Two optimum collectors were defined – RW9 and WK1. RW 9 is based on petroleum sulfonate and alkyl sulfosuccinate and is used for feldspar flotation. WK1 is a mixture of sodium alkyl sulfate, secondary amine, and sodium oleate modified with surfactant, which is is used for diopside and silica flotation. pH of 6 to 6.2 gave the best recovery/grade ratio results. Finally, the proposed flow sheet and reagent regime produced high-grade wollastonite with the recovery being above 80% (Bulatovic 2015).

Another research conducted by Siberian Federal University in Russia investigated possibility of recovering wollastonite and other valuable minerals from the tailings of Sinyukhinskoye gold mine located in the Republic of Altay (Russia) with the goal of utilizing the deposit in a more efficient way (Bragina and Konnova 2011). The wollastonite content in the tailings of this mine is between 20-30%, garnet – 20-30% and calcite is varied between 7-20%. As a result of this research, three stage flotation configuration with the high-gradient magnetic separation was proposed as indicated on Figure 18.

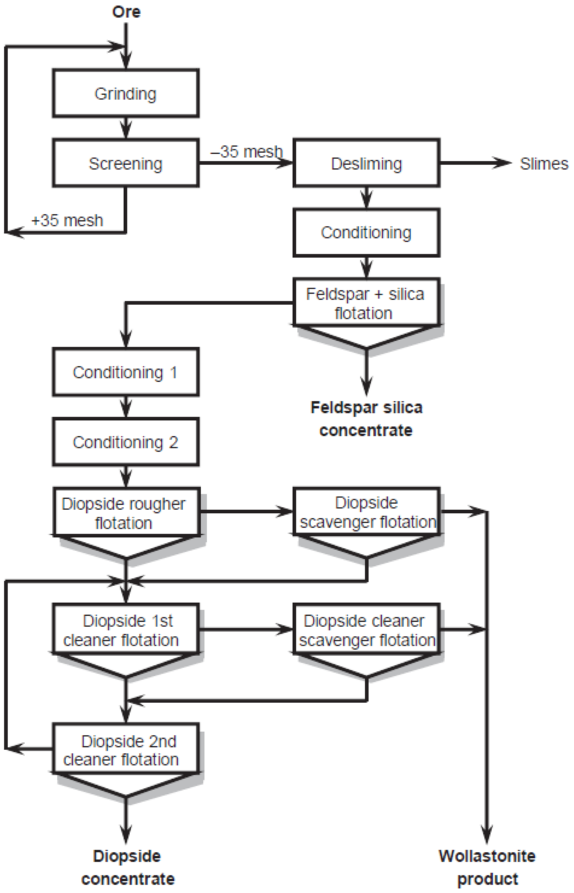


Figure 17. Two stage reverse flow sheet proposed for beneficiation of wollastonite ore (Bulatovic 2015).

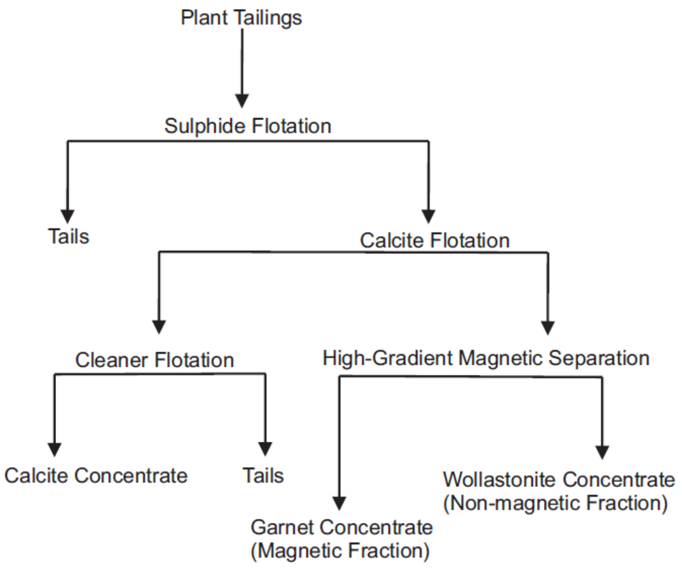


Figure 18. Proposed beneficiation flowsheet of the tailings of Sinyukhinskoye Mine in the Republic of Altay (Russia) (Bragina and Konnova 2011).

5. Design of Experiments

Design of experiments (DOE) is a branch of applied statistics that deals with planning, conducting, analyzing, and interpreting controlled experiments to evaluate the factors that affect the results, as well as optimize them to achieve the desirable output variables (responses).

In general terms, a designed experiment is the transformation of inputs into outputs. In the industrial context, inputs are factors or process variables such as process temperature, speed, dosage or even people, materials, methods, machines, etc. and outputs are considered as performance or quality characteristics of a product (Antony 2014).

When conducting a designed experiment, intentional changes to the input factors of a process are made in order to observe resulting changes in the process output. The information derived from correctly planned, executed and analyzed experiments can be utilized to optimize (improve) the process, for example, to increase recovery of valuable mineral from the ore, to increase quality of final product, to reduce excessive variability in production processes etc. (Antony 2014).

For better understanding, the DOE vocabulary definitions are described below:

- Factor (independent variable) - A controllable process, design or experimental variable to be tested (the x’s)
- Response (dependent variable) - The output or result (the y’s)
- Level - Specific value of the factor in the experimental run
- Design - Group of experimental runs to be performed and then statistically analyzed
- Run - One experimental test. A design is a series of runs.
- Repeats - Running the test again right away, taking an average that helps one to analyze for measurement error
- Replicates - Running the same experimental conditions more than once, rebuilding all conditions. Providing a measure of process error. Do not run sequentially if possible.
- Randomization - Running experiments in a random order to avoid the effects of lurking variables.

During the DOE multiple input factors and their combinations are considered and controlled simultaneously to ensure that the effects on the output responses are causal and statistically significant. It is important to note, that DOE provides maximum amount of information with minimum experiments.

The information which can be obtained with DOE is provided below:

1. Relationship between input and output factors.
2. Screening of important factors from unimportant.
3. Determination of interaction between input factors.
4. Prediction of possible output factors for any combination of variables based only on empirical results
5. Find optimum operating conditions.

There are two most popular experimental designs: factorial design and response surface. Each design is utilized in specific situations to gather information from a particular set of independent variables (Montgomery 2013).

5.1 Factorial Design

Factorial design is the most efficient for the study of effect of two or more factors. In factorial design, all probable combinations of the levels of the factors are studied in every complete trial of replicate of the experiment. For instance, in case there are *a* levels of factor A and *b* levels of factor B, each trial includes all *ab* treatment combinations. Factors organized in a factorial design are often said to be crossed (Montgomery 2013).

The change in response created by a change in the level of factor is set to be the effect of the factor. This is usually considered as the main effect as it refers to the primary factors of interest in the experiment. Two-factor factorial experiment can be seen from Figure 11, which has both design factors at two levels. These levels are named “low” and “high” and noted as “+” and “-,” respectively. The primary effect of factor A in this design is considered as the difference between the average response at the low level of A and the average response at the high level of A. Mathematically, this is

$$A = \frac{40 + 52}{2} - \frac{20 + 30}{2} = 21 \tag{5.1}$$

Therefore, increasing factor A from the low level to the high level creates an average response increase of 21. Correspondingly, the main effect of B is

$$B = \frac{30 + 52}{2} - \frac{20 + 40}{2} = 11 \tag{5.2}$$

If the factors are provided at more than two levels, this formula should be modified because there are other ways to describe the effect of a factor (Montgomery 2013).

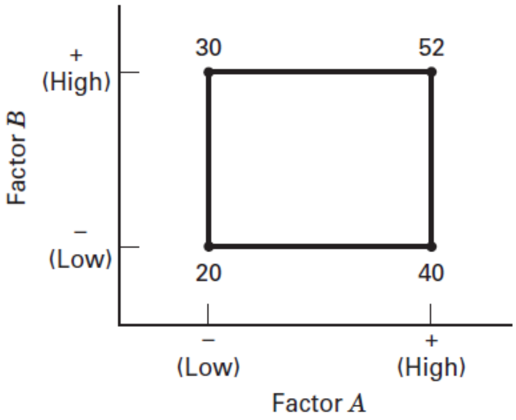


Figure 19. A two-factor factorial experiment, where the response (y) presented at the corners (Montgomery 2013).

Many experiments have the difference in response between the levels of one factor being different at all levels of the other factors. In such situations, there is an interaction between the factors. For example, in two-factor factorial experiment provided in Figure 19. At the low level of factor B, the effect of A is

$$A = 50 - 20 = 30 \tag{5.3}$$

and at the high level of factor B, the effect of A is

$$A = 12 - 40 = -28 \tag{5.4}$$

As you it can be seen, the effect of A is affected by the chosen level of factor B, which means that there is interaction between A and B. The magnitude of the interaction effect should be considered as the average difference in these two A effects, or AB = (–28 – 30)/2 = – 29. Apparently, the interaction is significant in the experiment (Montgomery 2013).

Overall, factorial design has several advantages. It is more efficient than one-factor-at-a-time experiment as it requires less experimental runs with the same precision of results. Moreover, a factorial design is essential to analyze any present interactions to avoid misleading conclusions. Finally, factorial design estimates the level of a factor at several levels of the other factors, providing conclusions that are accurate over a range of experimental conditions (Antony 2014).

5.2 Response Surface Methodology

Response surface methodology (RSM) is the most commonly used statistical experimental design method used for optimization purposes. RSM is defined as a collection of statistical and mathematical methods for modelling and analyzing the relationship between the input factors and the output variables with the main objective to optimize the process through developing a second order mathematical model and representing the direct and interactive effects through two and three-dimensional plots (Kökkılıç, Langlois et al. 2015).

The objectives of RSM are provided below (Sarabia and Ortiz 2009):

- To obtain information in the experimental domain of interest.
- To reliably estimate the experimental bias (pure error).
- To ensure the accuracy between the proposed model and the experimental data.
- To predict the obtained response, as statistically precise as possible.
- To model sequential strategies to conduct the experimentation with different conditions according to the results obtained.
- To maintain a high efficiency in terms of economical costs, time, and any other limitations.
- To easily identify the outlying data.
- To allow decision making under uncertain conditions, reducing the ambiguity.

The two-level factorial designs are modeled linearly, which means the output response surfaces in three-dimensional space are flat or twisted planes if the interactions present. Adding a center point into the two-factorial model can be helpful for monitoring the curvature. However, response surfaces frequently exhibit significant curvature and for that condition, RSM is the best method to utilize (Eyjolfsson 2015).

In most RSM employed experiments, the shape of the relationship between the response and the independent variables is unknown. Therefore, the initial stage in RSM is to define a suitable approximation for the actual functional relationship between y and the set of independent variables. Basically, a low-order polynomial in some region of the independent variables is utilized. If the response is correctly modeled by a linear function of the independent variables, then the approximating function is the first-order model.

$$y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \cdots + \beta_k x_k + \epsilon \tag{5.2.1}$$

If there is curvature in the system, in that case a polynomial of higher degree should be utilized, such as the second-order model

$$y = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \beta_{ii} x_i^2 + \sum\sum_{i<j} \beta_{ij} x_i x_j + \epsilon \qquad (5.2.2)$$

Practically all RSM problems utilize one or both of these models. Definitely, it is improbable to have polynomial model to be reasonable approximation of the actual functional relationship over the full space of the independent variables, however for a comparably small area they commonly work well (Montgomery 2013).

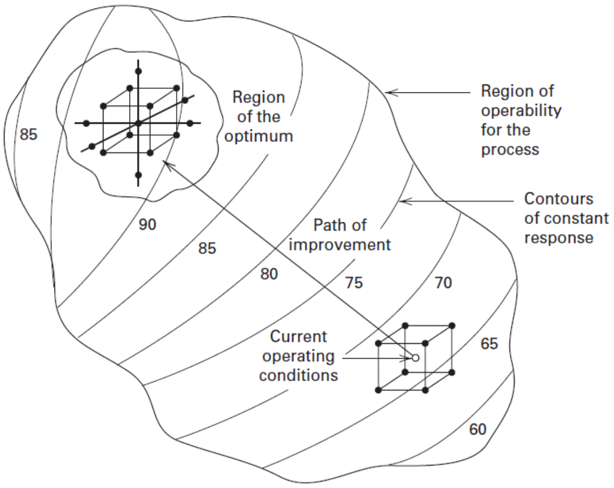


Figure 20. A two-factor factorial experiment, where the response (y) presented at the corners (Montgomery 2013).

It is important to note that RSM is a sequential procedure. In situations when we are located in the area on the response surface that is distant from the optimum, as indicated in Figure 20 (current operating conditions), there is little curvature in the system and the first-order model will be suitable. The goal here is to lead the experimenter quickly and efficiently along a path of improvement toward the general area of the optimum. As the area of the optimum has been detected, a more complex second-order model may be utilized, and an analysis may be conducted to find the optimum. It can be observed from Figure 20 that the analysis of a response surface can be seen of as “climbing a hill,” where the top of the hill portrays the point of maximum response and if the actual optimum is a point of minimum response, then we may see it as “descending into a valley” (Montgomery 2013).

The final goal of RSM is to identify the optimum operating conditions for the system or to identify factor area in which operating requirements are satisfied.

6. Methodology

6.1 Materials

6.1.1 Minerals

Considering that wollastonite ore of Saint Lawrence Mine consist of primarily wollastonite, diopside and other silicate minerals (Table 2), which have insignificant difference in specific gravities (wollastonite – 2.86–3.09, diopside – 3.25-3.55) as well as similar diamagnetic and electrostatic properties, reverse flotation is considered as an optimum method of beneficiation of this ore.

Therefore, wollastonite ore containing 36-37% wollastonite and 30-31% diopside (Table 3) have been used for batch flotation tests, which was received from Saint Lawrence Mine (Ontario) owned by Canadian Wollastonite.

Table 2. Grade estimation of the feed sample

Overall Grade %					
Diopside	**Wollastonite**	**Fe-Diopside**	**K-Ortho**	**Na-Albite**	**Quartz**
30.29	36.47	1.47	9.28	9.63	9.04

First, incoming ore was treated by hydrocycloning in order to remove fine size fraction of -38 μm, which has been proved to have low selectivity during flotation. Then, the ore was split on the rotary splitter into homogenous 1 kg bags.

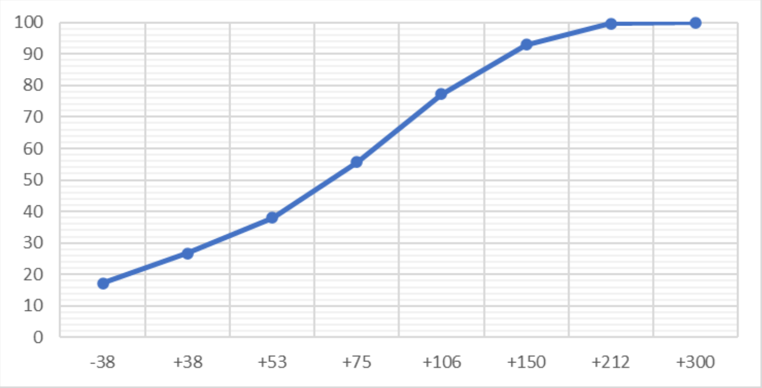


Figure 21. Size distribution of wollastonite ore used in the flotation tests.

After that, three random samples were taken for screen analysis at 212 μm, 150 μm, 106 μm, 75 μm, 54 μm and 38 μm in order to confirm homogeneity of the ore. Screen analysis results can be seen from Table 3 and Figure 21, the calculated P_{80} is 112 μm. Finally, the ore was characterized using Quantitative Evaluation of Minerals by Scanning Electron Microscopy (QEMSCAN) and X-ray fluorescence (XRF).

Table 3. Size distribution of wollastonite ore used in the flotation tests.

Size (um)	**Mass (g)**	**Mass (%)**	**Cum. Passing (%)**
+300	0.91	0.36	100.00
+212	17.00	6.64	99.64
+150	40.54	15.82	93.01
+106	54.95	21.45	77.18
+75	45.45	17.74	55.74
+53	28.77	11.23	38.00
+38	24.44	9.54	26.77
-38	44.13	17.23	17.23
TOTAL	256.19	100	

6.1.2 Reagents

Six collector agents have been used in the test to achieve desirable diopside flotation results – B-400, HT, CA-250 and CA-375 produced by NORDCHEM, as well as R855, R845 produced by Cytec. Also, PAX was used as a sulfide collector and MIBC as a frothing agent.

Collectors B-400, HT, CA-250 and CA-375 are grouped into one WK6 collector, and collectors R855 and R845 are mixed into RW9. Reagent recipes for the experiment are taken from Handbook of Flotation Reagents by Srdjan M. Bulatovic.

6.2 Design of Experiments (DOE)

The wollastonite flotation conditions were developed using response surface methodology (RSM) and central composite design (CCD). The main purpose of using CCD is to investigate the relationship between independent input factors (flotation reagents) and response parameters (grade and recovery), possible interactions between them, as well as their effects on the wollastonite flotation process in an efficient and accurate way.

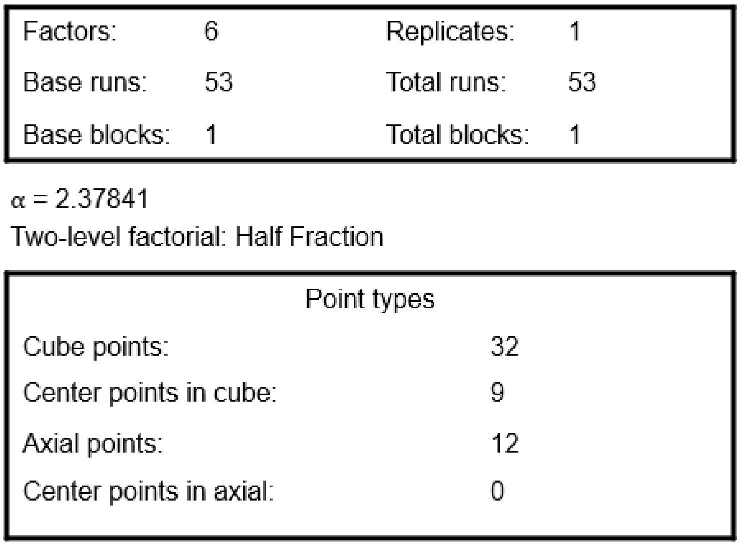
Six experimental input factors including the dosages of B-400, HT, CA-375, CA-250, R855 and R845 were selected as the main factors. The coded and corresponding actual values of variables are provided in Table 4.

Based on CCD parameters (Table 5), 53 experimental reagent recipes were generated in a randomized order (Appendix A). All calculations were performed using Minitab software.

Table 4. Independent variables and their levels

Variable	**Agreed % in Solution for center level**	**Coded variable level**		
		Low - α	**Center 0**	**High +α**
B-400	4.3	0	12.9	25.8
HT	31.9	0	95.7	191.4
CA-375	31.9	0	95.7	191.4
CA-250	31.9	0	95.7	191.4
R855	67	0	201	402
R845	33	0	99	198

Table 5. Parameters of utilized Central Composite Design (CCD)



```
Factors:        6          Replicates:     1
Base runs:      53         Total runs:     53
Base blocks:    1          Total blocks:   1

α = 2.37841
Two-level factorial: Half Fraction

                  Point types
Cube points:                      32
Center points in cube:            9
Axial points:                     12
Center points in axial:           0
```

6.3 Batch Flotation Tests

Batch flotation tests were conducted in a 1.5 L Denver laboratory flotation cell. The slurry density - 24%, pH – 8.5, impeller speed – 1200 rpm and the air flow rate - 2.8 l/min. Impeller speed and air flow rate were determined empirically. The test is conducted using tap water.

First, 2 ml of 1% Potassium amyl xanthate (PAX), as well as Methyl isobutyl carbinol (MIBC) are added to the process as a collector of sulphide minerals and frothing agent respectively.

Then, after 1 minute of conditioning, sulphide flotation is conducted where sulphide concentrate is floated. The main purpose of this stage is to clean the slurry from Sulphur containing minerals. Then, 2 ml of acetic acid is added to the process as a depressor of wollastonite for the subsequent diopside flotation. After 3 minutes of conditioning, RW9 and WK6 reagents are added to the process in various amount depending on specific DOE recipe (Appendix A). After another 3 minutes of conditioning, diopside flotation is conducted for 3 minutes, where diopside concentrate is floated and wollastonite concentrated is produced in the sink. During this stage, a total of 7 separate diopside concentrate portions are collected for each test at 15 s, 30 s, 60 s, 90 s, 120 s, 150 s and 180 s with the eventual goal to analyze kinetics of diopside flotation.

7. Results and Discussions

The resulting experimental grades of sink material can be seen from Appendix B. There are 8 elemental analysis results conducted by Techni-Lab S.G.B. Abitibi Inc., Ste-Germaine Boulé, Quebec, as well as wollastonite and diopside mineral grades calculated using formulas provided below.

Diopside = MgO/17.2*100

Wollastonite = (CaO-(MgO/17.2*25.9))/48.3*100

Based on the feed grade as well as the mass of sink and floated material overall recoveries of diopside and wollastonite have been calculated and provided in Appendix C. Diopside recoveries and concentrate grades for all 53 DOE runs are presented in the Figure 22.

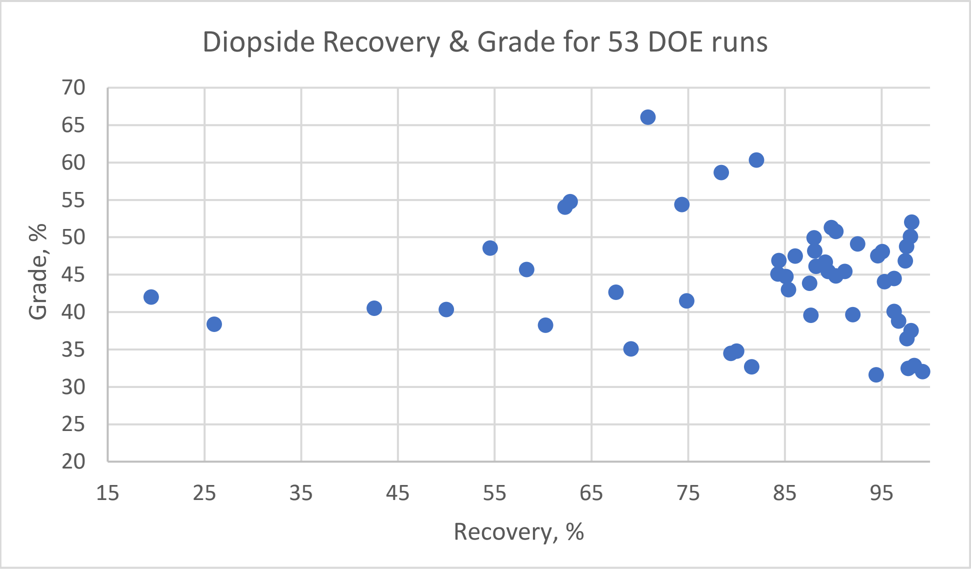


Figure 22. Diopside recoveries and concentrate grades for all 53 DOE runs.

Based on the calculated recoveries of wollastonite and diopside, analysis of input variables has been run in Minitab. Standardize effects of the input variables for the optimum wollastonite recovery to sink material can be seen from Figure 22. Standardize effects of the input variables for the diopside recovery to floated material is provided in Figure 23. Regression equations are provided in Appendix D.

Regarding diopside recovery, there are 8 input factors, which can be considered statistically significant, while for wollastonite recovery, there are only 2 input factors, which can be considered as statistically significant (B-400 and combination of B-400 with R855).

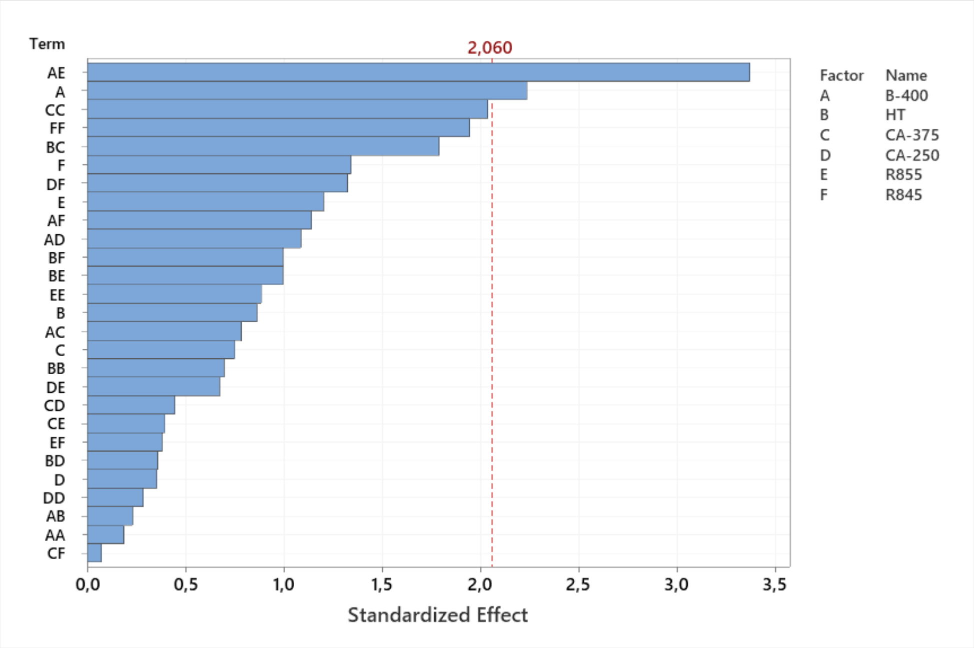


Figure 23. Pareto chart of the standardized effects – wollastonite recovery to sink

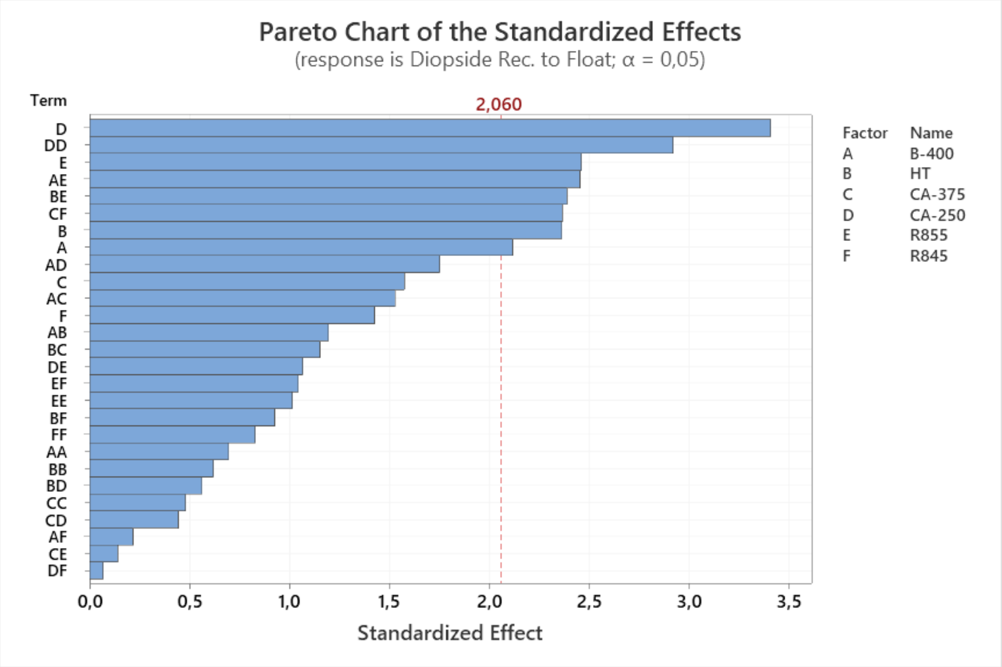


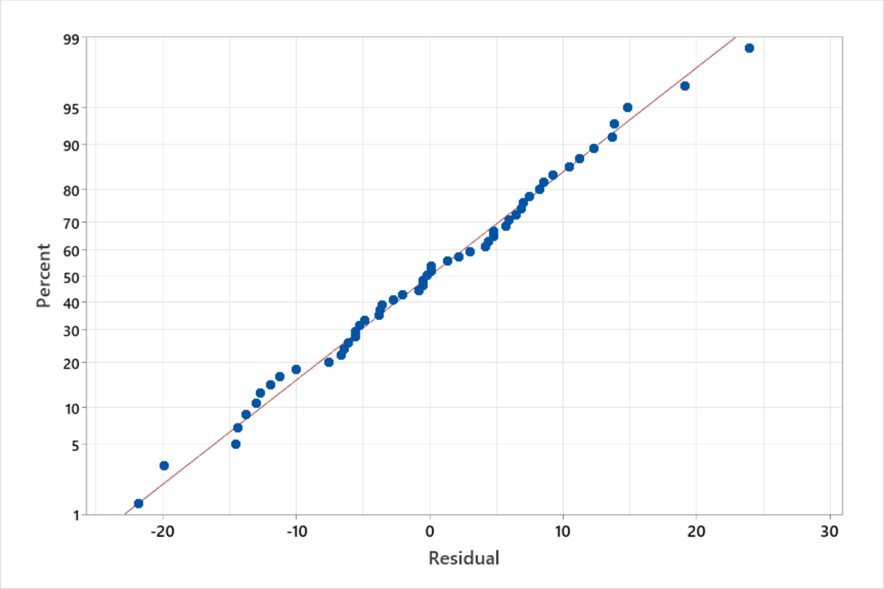
Figure 24. Pareto chart of the standardized effects – diopside recovery to float.

In order to estimate the significance of the developed models, ANOVA was applied as shown in Table 6. The calculated F-values of diopside and wollastonite recoveries are 2.24 and 2.01 respectively, both higher than the F value from the F-statistics Table, with P=0.05 ($F_{0.05(27,25)}$ = 1.93). Therefore, it can be concluded that the regression models are considered acceptable and fit well. Moreover, the p-values (P) of the regression models which are 0.023 for diopside recovery and 0.042 for wollastonite recovery are lower than 0.05, consequently these models are considered statistically significant and suitable for modelling the response behaviors.

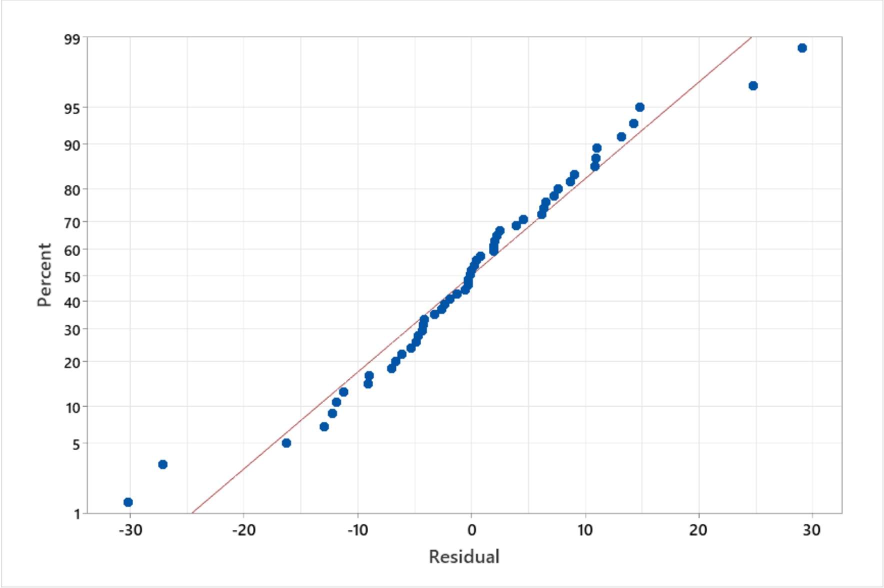
Table 6. ANOVA for diopside and wollastonite recoveries.

Source	DF	Diopside Recovery to Float				Wollastonite Recovery to Sink			
		Adj SS	Adj MS	F-Value	P-Value	Adj SS	Adj MS	F-Value	P-Value
Model	27	12189,0	451,44	2,24	0,023	12598,9	466,63	2,01	0,042
Linear	6	3940,7	656,79	3,26	0,016	2320,4	386,74	1,67	0,171
B-400	1	897,9	897,89	4,46	0,045	1380,1	1380,13	5,94	0,022
HT	1	1123,4	1123,44	5,58	0,026	63,9	63,86	0,28	0,605
CA-375	1	497,7	497,72	2,47	0,128	92,7	92,69	0,40	0,533
CA-250	1	2339,2	2339,17	11,63	0,002	0,0	0,00	0,00	1,000
R855	1	1217,6	1217,57	6,05	0,021	438,6	438,56	1,89	0,182
R845	1	409,1	409,14	2,03	0,166	538,5	538,54	2,32	0,140
Square	6	2258,2	376,37	1,87	0,126	2392,3	398,72	1,72	0,158
B-400*B-400	1	97,6	97,65	0,49	0,492	3,1	3,09	0,01	0,909
HT*HT	1	77,4	77,37	0,38	0,541	95,5	95,46	0,41	0,527
CA-375*CA-375	1	46,6	46,57	0,23	0,635	946,1	946,14	4,07	0,054
CA-250*CA-250	1	1716,8	1716,85	8,53	0,007	31,6	31,62	0,14	0,715
R855*R855	1	207,2	207,22	1,03	0,320	161,7	161,71	0,70	0,412
R845*R845	1	138,5	138,50	0,69	0,415	998,2	998,20	4,30	0,049
2-Way Interaction	15	5869,8	391,32	1,94	0,068	6226,6	415,11	1,79	0,096
B-400*HT	1	288,0	287,97	1,43	0,243	96,0	96,00	0,41	0,526
B-400*CA-375	1	469,8	469,78	2,33	0,139	339,8	339,83	1,46	0,238
B-400*CA-250	1	618,1	618,11	3,07	0,092	117,7	117,67	0,51	0,483
B-400*R855	1	1211,4	1211,35	6,02	0,021	3471,6	3471,55	14,95	0,001
B-400*R845	1	9,6	9,57	0,05	0,829	577,9	577,95	2,49	0,127
HT*CA-375	1	267,7	267,71	1,33	0,260	477,5	477,46	2,06	0,164
HT*CA-250	1	63,9	63,87	0,32	0,578	0,3	0,30	0,00	0,972
HT*R855	1	1148,5	1148,55	5,71	0,025	88,4	88,40	0,38	0,543
HT*R845	1	172,8	172,78	0,86	0,363	88,5	88,52	0,38	0,543
CA-375*CA-250	1	39,7	39,70	0,20	0,661	173,3	173,27	0,75	0,396
CA-375*R855	1	4,0	3,99	0,02	0,889	0,0	0,00	0,00	0,999
CA-375*R845	1	1126,6	1126,56	5,60	0,026	53,4	53,39	0,23	0,636
CA-250*R855	1	229,0	229,02	1,14	0,296	19,1	19,15	0,08	0,776
CA-250*R845	1	1,0	0,95	0,00	0,946	723,1	723,08	3,11	0,090
R855*R845	1	219,9	219,90	1,09	0,306	0,0	0,05	0,00	0,989
Error	25	5030,2	201,21			5804,8	232,19		
Lack-of-Fit	17	4704,9	276,76	6,81	0,005	5519,5	324,68	9,10	0,002
Pure Error	8	325,2	40,66			285,3	35,66		
Total	52	17219,2				18403,7			

DF = degrees of freedom, Seq SS = sequential sums of squares, Adj MS = Adjusted mean squares



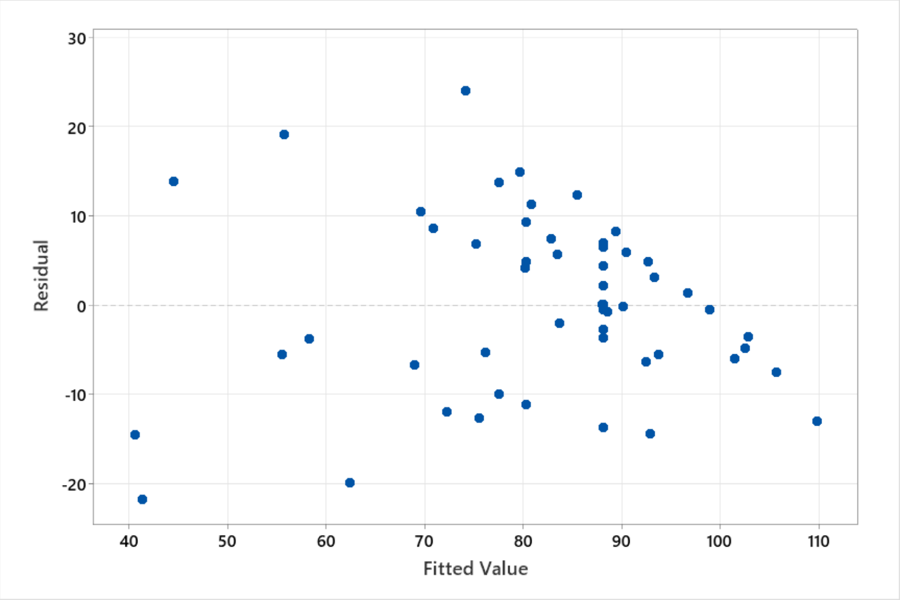
(a) Normal probability plot of residuals for diopside recovery to float.



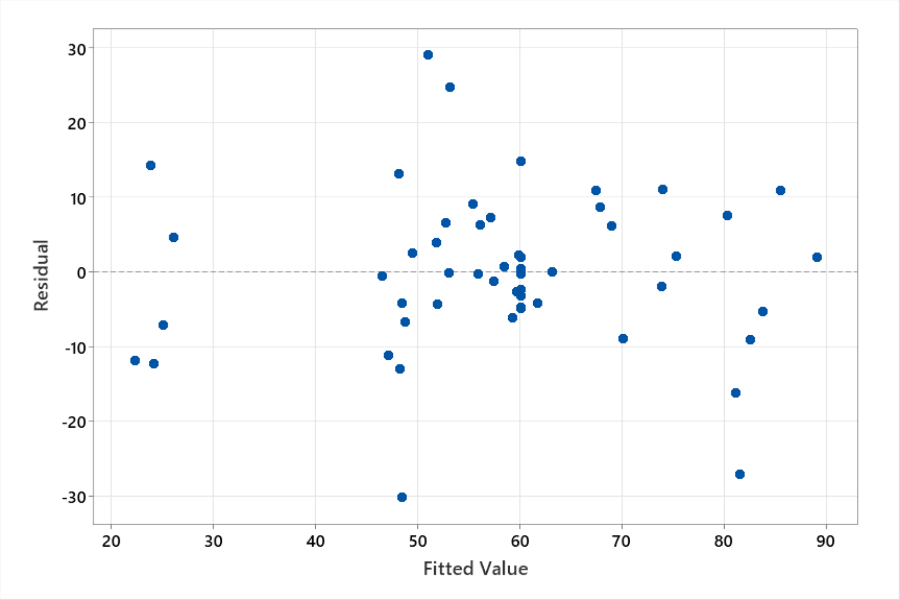
(b) Normal probability plot of residuals for wollastonite recovery to sink.

Figure 25. Normal probability plots for (a) diopside recovery to float and (b) wollastonite recovery to sink.

The normal probability plot of the residuals and the plot of the residuals versus the predicted response for both diopside recovery to float and wollastonite recovery to sink are presented in Figure 25 and Figure 26, respectively. Figure 25 shows that the residuals generally lie on a straight line, which indicates that errors are distributed normally. From Figure 26 it can be seen that the residuals scatter randomly, suggesting that the predictions of the models are adequate.



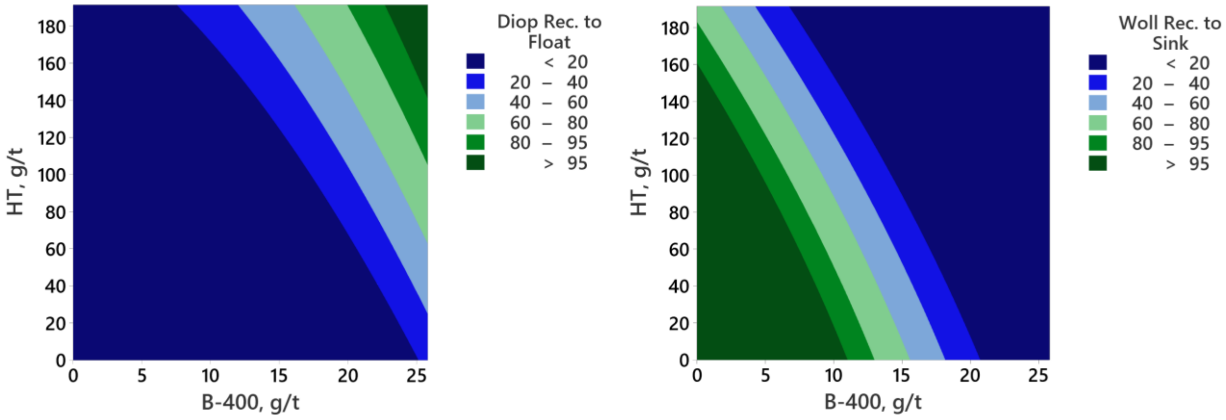
(a) Plot of residuals versus fitted response for diopside recovery to float.



(b) Plot of residuals versus fitted response for wollastonite recovery to sink.

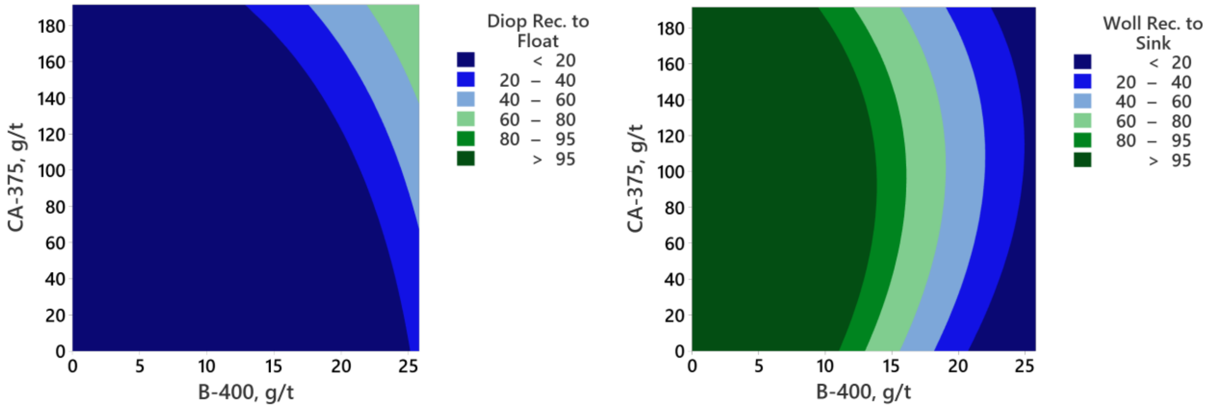
Figure 26. Plot of residuals versus predicted response for (a) diopside recovery to float and (b) wollastonite recovery to sink

Furthermore, based on the RSM 2-dimensional contour plots have been created in order to evaluate direct and indirect relationships between various input factors and their effect on output variables.



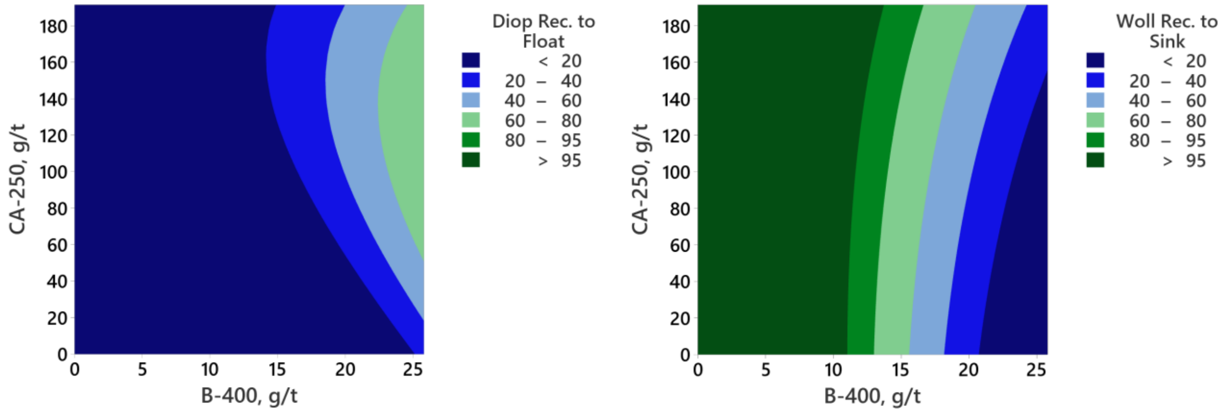
(a) (b)

Figure 27. Response surface plots of the effect of HT and B-400 combination on the recoveries of (a) diopside to float and (b) wollastonite to sink.



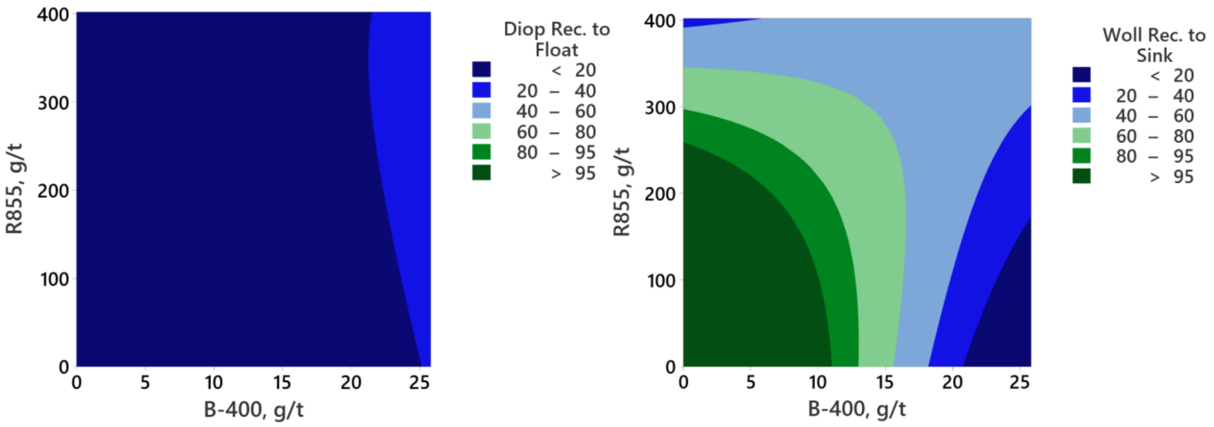
(a) (b)

Figure 28. Response surface plots of the effect of CA-375 and B-400 combination on the recoveries of (a) diopside to float and (b) wollastonite to sink.



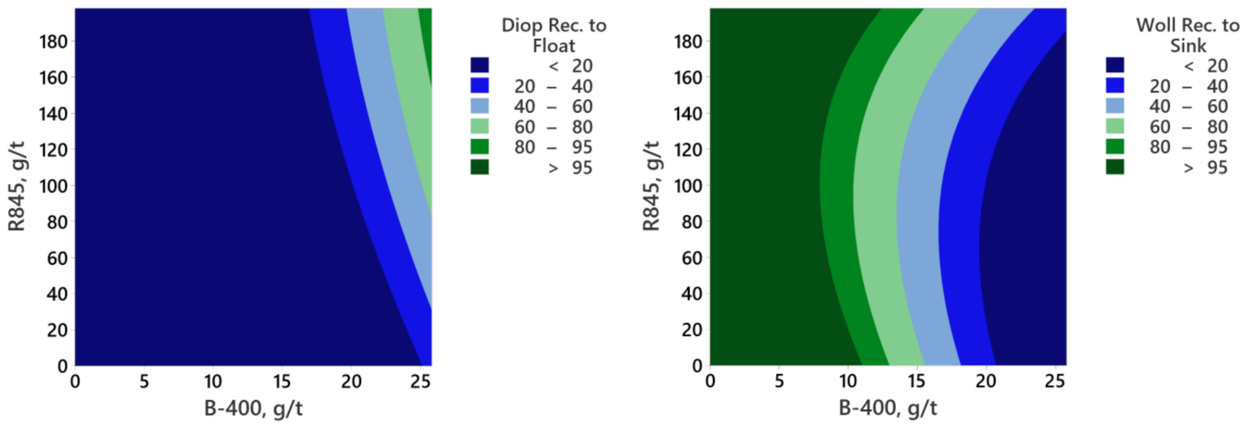
(a) (b)

Figure 29. Response surface plots of the effect of CA-250 and B-400 combination on the recoveries of (a) diopside to float and (b) wollastonite to sink.



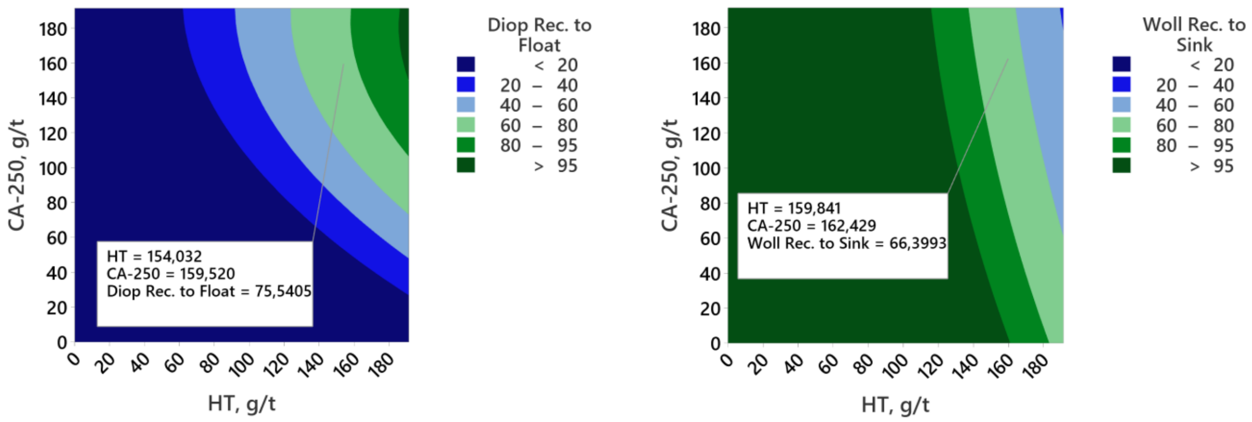
(a) (b)

Figure 30. Response surface plots of the effect of R855 and B-400 combination on the recoveries of (a) diopside to float and (b) wollastonite to sink.



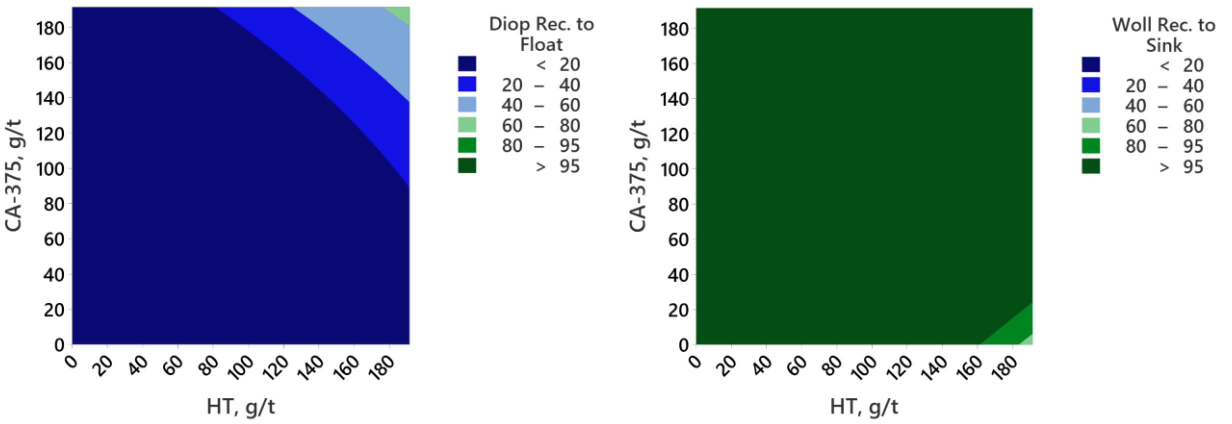
(a) (b)

Figure 31. Response surface plots of the effect of R845 and B-400 combination on the recoveries of (a) diopside to float and (b) wollastonite to sink.



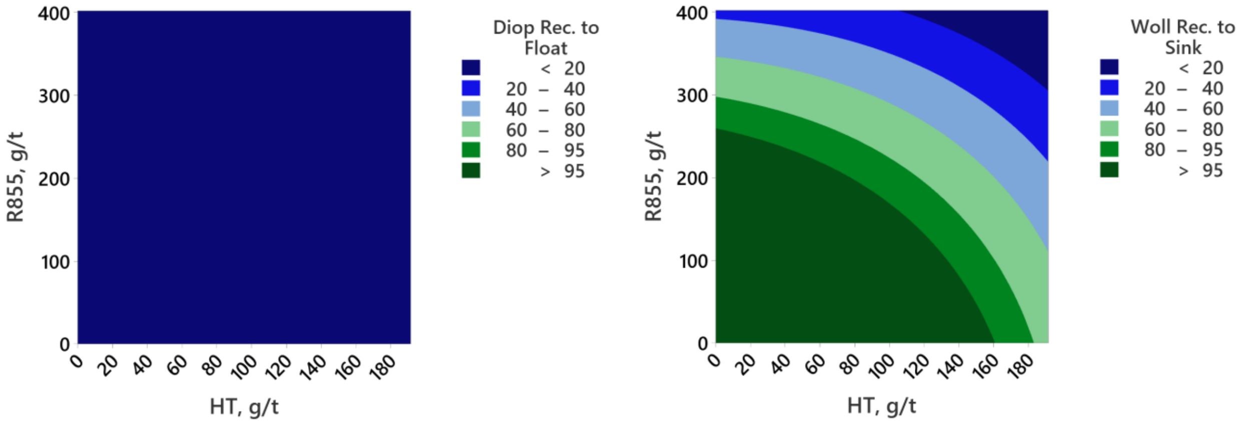
(a) (b)

Figure 32. Response surface plots of the effect of CA-250 and HT combination on the recoveries of (a) diopside to float and (b) wollastonite to sink.



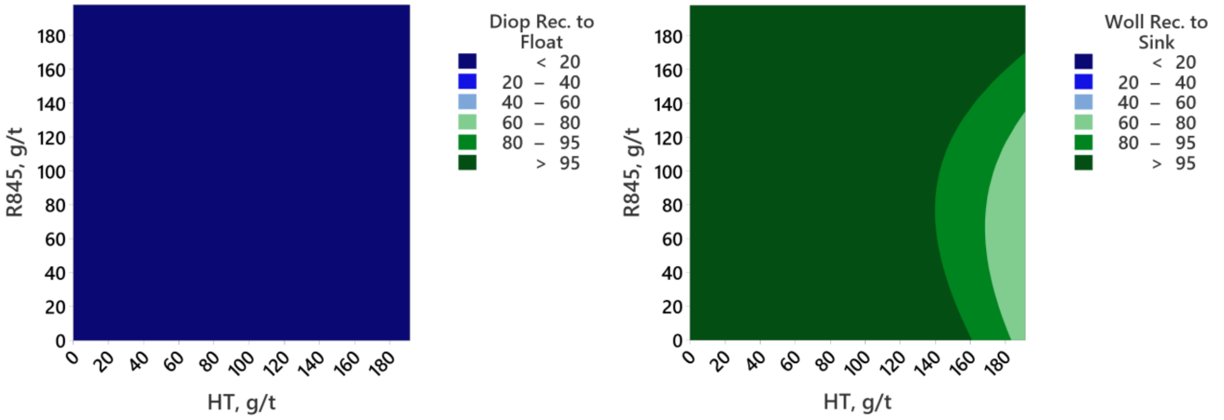
(a) (b)

Figure 33. Response surface plots of the effect of CA-375 and HT combination on the recoveries of (a) diopside to float and (b) wollastonite to sink.



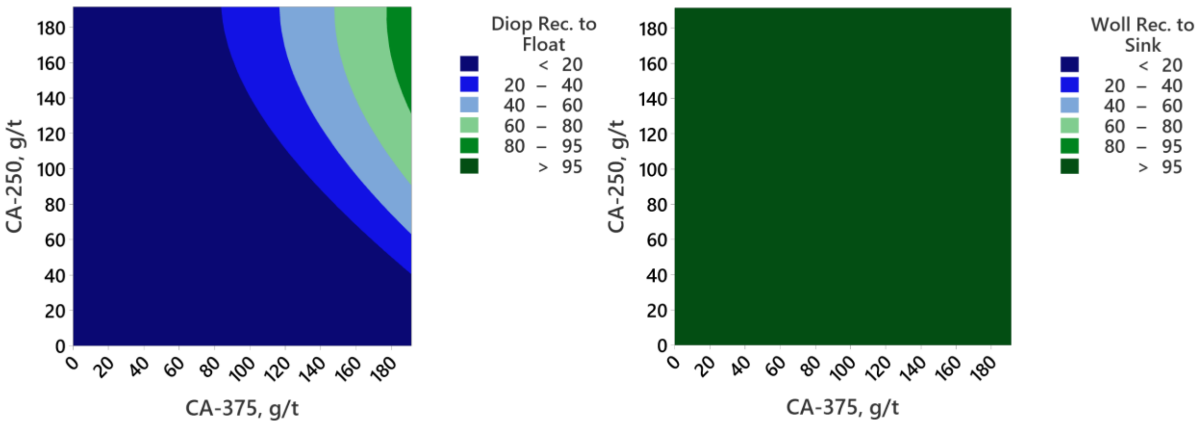
(a) (b)

Figure 34. Response surface plots of the effect of R855 and HT combination on the recoveries of (a) diopside to float and (b) wollastonite to sink.



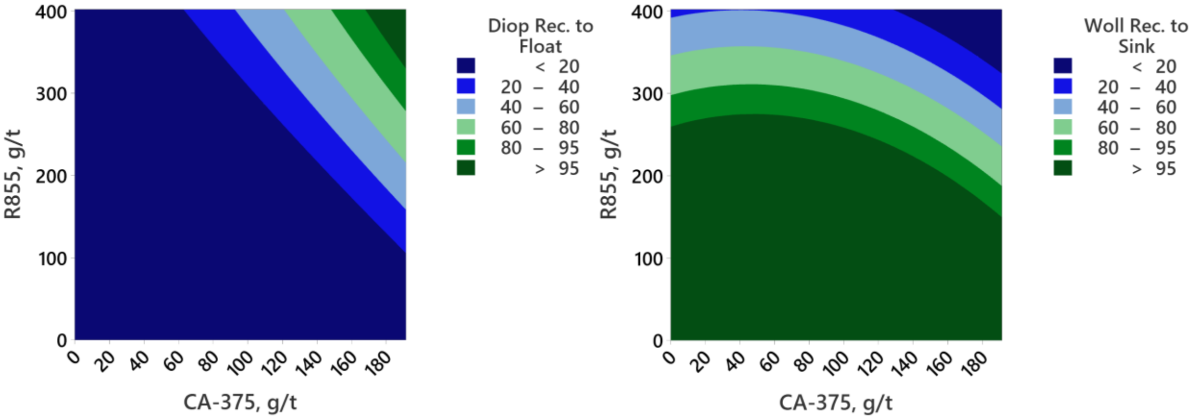
(a) (b)

Figure 35. Response surface plots of the effect of R845 and HT combination on the recoveries of (a) diopside to float and (b) wollastonite to sink.



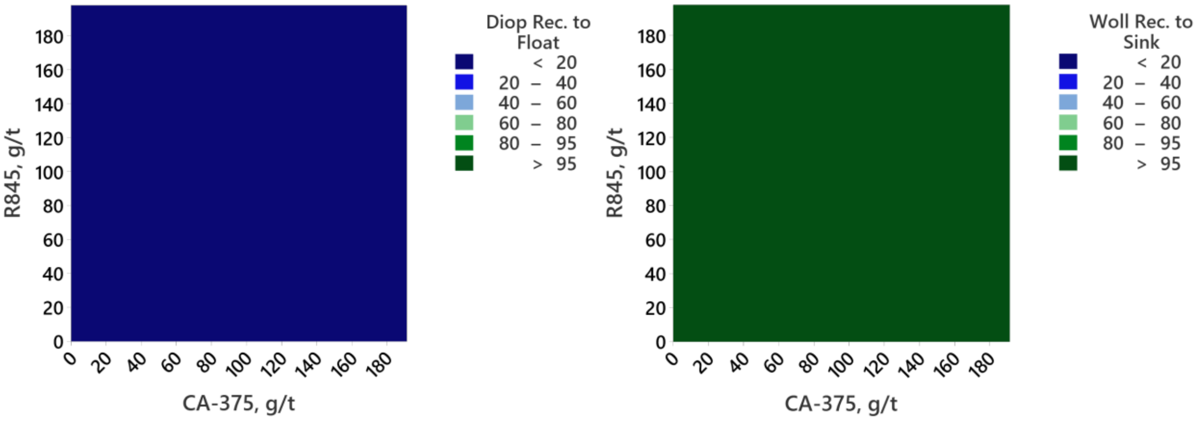
(a) (b)

Figure 36. Response surface plots of the effect of CA-250 and CA-375 combination on the recoveries of (a) diopside to float and (b) wollastonite to sink.



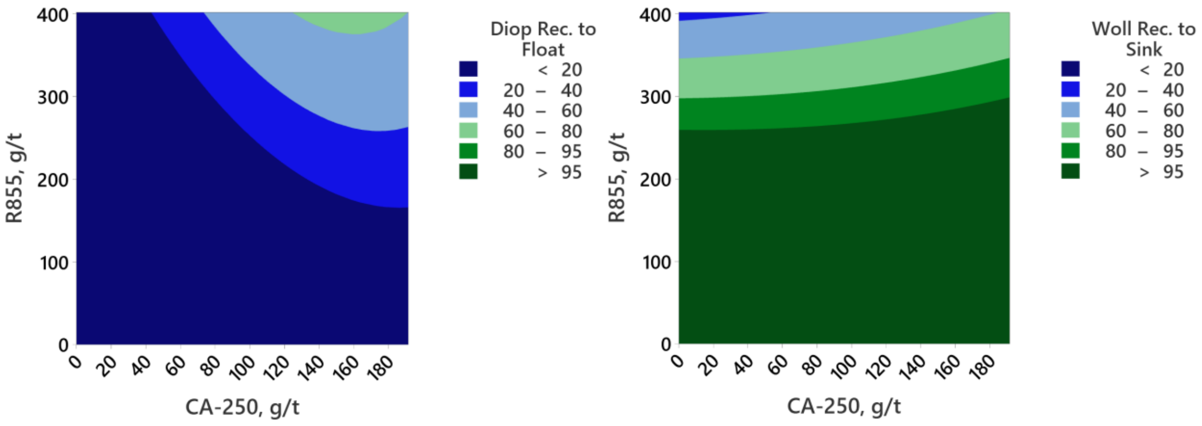
(a) (b)

Figure 37. Response surface plots of the effect of R855 and CA-375 combination on the recoveries of (a) diopside to float and (b) wollastonite to sink.



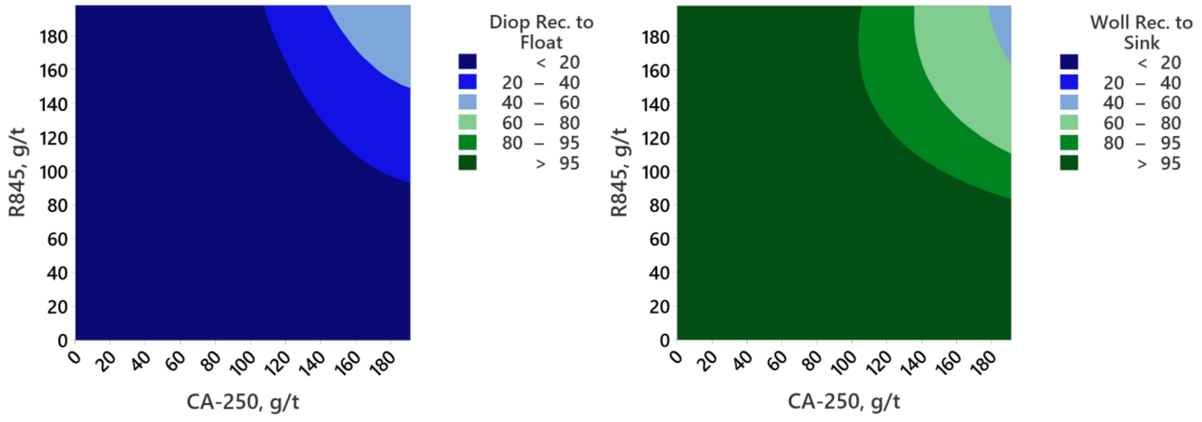
(a) (b)

Figure 38. Figure 36. Response surface plots of the effect of R845 and CA-375 combination on the recoveries of (a) diopside to float and (b) wollastonite to sink.



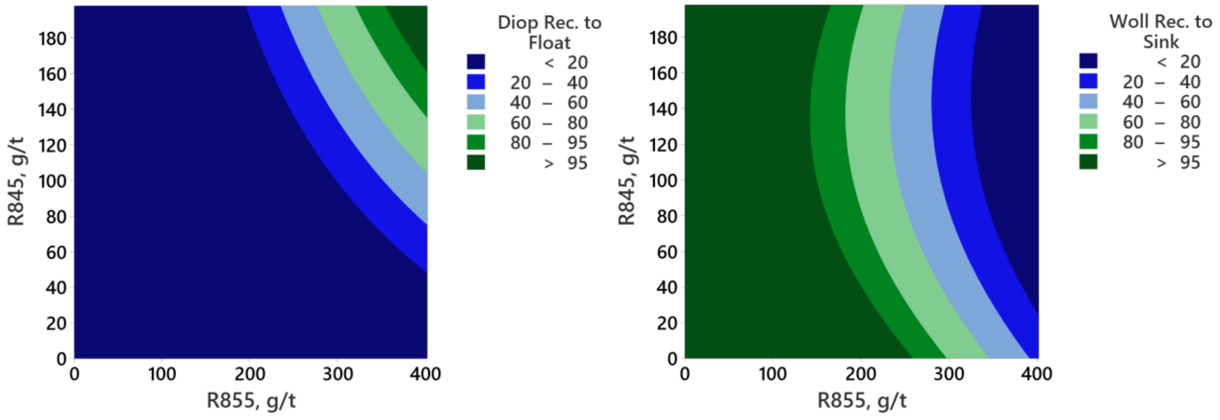
(a) (b)

Figure 39. Response surface plots of the effect of R855 and CA-250 combination on the recoveries of (a) diopside to float and (b) wollastonite to sink.



(a) (b)

Figure 40. Response surface plots of the effect of R845 and CA-250 combination on the recoveries of (a) diopside to float and (b) wollastonite to sink.



(a) (b)

Figure 41. Response surface plots of the effect of R845 and R855 combination on the recoveries of (a) diopside to float and (b) wollastonite to sink.

As it can be seen from Figure 27 (a), combination of HT and B-400 provides high productivity for diopside recovery to float, however, if we look at Figure 27 (b), it becomes obvious that this combination provides non-selective recovery of both wollastonite and diopside to the float.

Moreover, all reagent combinations with B-400 result in low separation efficiency (Figure 28, 29, 30, 31), both valuable minerals are either recovered to the concentrate or to the tails depending on the dosage. Therefore, it is recommended to avoid using B-400 in any combination for this flotation process.

At the same time, combination of HT and CA-250 (Figure 32) showed good results. Statistically both diopside and wollastonite recoveries of 60-80% can be achieved at high dosages of CA-250 and HT. However, excessively high dosage of HT leads to low recovery of wollastonite to the sink, which negatively affects diopside concentrate grade. Apparently, HT has an enforcing property for CA-250 to some extent.

Combination of HT with CA-375 (Figure 33) provides recoveries of both minerals at around 60% at the maximum dosages of both reagents. Combination of HT with the rest of the reagents (Figure 34, 35) displays low recoveries of diopside to the float (below 20%) regardless of dosages. Consequently, HT can enhance CA-375 (as CA-250) collecting properties when used in moderate dosages.

CA-250 and CA-375 is the best combination among all other combinations in terms of separation efficiency (Figure 36). Statistically, diopside recovery to float of above 80% and wollastonite recovery to sink of above 95% are achieved at high dosages of both reagents. This regent combination provides high selectivity for diopside recovery as with the increase in the diopside recovery to float, wollastonite recovery to sink does not change remaining in the above 95% range.

All contour plots show that R855 show weak separation efficiency in all of the combinations (Figure 37, 38, 39, 40, 41). R845 plays some role in reaching higher recovery of diopside and wollastonite to their concentrate phases. Its dosage should depend on the dosages of CA-375 and probably CA-250. The usage of CA-375 might lower the dosage of R845. Overall, R855 and R845 should be used as low as possible or shouldn’t be used at all.

Further, in order to calculate the best operating conditions within the system, response optimization has been run with the objective of maximizing diopside recovery to float and wollastonite recovery to sink. Response optimization results are provided in Table 7.

Table 7 Statistically optimum input factors to reach maximum recoveries of diopside to float and wollastonite to sink.

B-400	**HT**	**CA-375**	**CA-250**	**R855**	**R845**
		g/t			
0.0	15.7	191.4	191.4	0.0	10.1

According to optimization results, to reach maximum recoveries of diopside to float and wollastonite to sink, collectors CA-375, CA-250 should be used at maximum dosages of 191.4 g/t each, while HT and R845 at the low dosages of 15.7 g/t and 10.1 g/t respectively. B-400 and R855 should not be utilized at all.

Overall, based upon the optimization results, using the optimized combination of input variables, maximum recoveries of diopside to float and wollastonite to sink of above 90% can be achieved.

8. Conclusions

- Statistically significant input factors for diopside and wollastonite recoveries have been identified with the use of RSM. There are 8 statistically significant input factors affecting diopside recovery to floated material and 2 significant factors affecting wollastonite recovery to sink.
- B-400 and R855 exhibited strong non-selective collecting properties, while CA-375 and CA-250 showed highly selective collecting properties. HT and B855 displayed some enforcing behavior in some combinations with CA-250, however acted weakly in other combinations.
- Based on the RSM, optimum operating conditions to reach maximum possible recoveries of above 90% have been derived - collectors CA-375, CA-250 should be used at maximum dosages of 191.4 g/t each, while HT and R845 at the low dosages of 15.7 g/t and 10.1 g/t respectively. B-400 and R855 should not be utilized at all.

9. Future work

- Conducting further cleaning stages to separate quartz/feldspars from the wollastonite and diopside concentrates to increase the grades to marketable ranges.
- Optimize other flotation variable such as flotation kinetics, impeller speed and flotation cell configuration using design of experiments (DOE).
- Evaluate efficiency of using flotation columns and reactors to achieve higher flotation efficiency.
- Test modern reagents, which were recently developed for silicate flotation to enhance recoveries, grades or overall kinetics.

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Appendix A. Central Composite Design Recipes of the Experiment.

DOE		WK-6, g/t				RW-9, g/t	
StdOrder	**RunOrder**	**B-400**	**HT**	**CA-375**	**CA-250**	**R855**	**R845**
47	1	12.90	95.70	95.70	95.70	201.00	99.00
1	2	7.48	55.46	55.46	55.46	116.49	57.38
35	3	12.90	0.00	95.70	95.70	201.00	99.00
44	4	12.90	95.70	95.70	95.70	201.00	198.00
39	5	12.90	95.70	95.70	0.00	201.00	99.00
46	6	12.90	95.70	95.70	95.70	201.00	99.00
32	7	18.32	135.94	135.94	135.94	285.51	140.62
33	8	0.00	95.70	95.70	95.70	201.00	99.00
6	9	18.32	55.46	135.94	55.46	116.49	57.38
49	10	12.90	95.70	95.70	95.70	201.00	99.00
38	11	12.90	95.70	191.40	95.70	201.00	99.00
45	12	12.90	95.70	95.70	95.70	201.00	99.00
11	13	7.48	135.94	55.46	135.94	116.49	57.38
42	14	12.90	95.70	95.70	95.70	402.00	99.00
2	15	18.32	55.46	55.46	55.46	116.49	140.62
7	16	7.48	135.94	135.94	55.46	116.49	57.38
28	17	18.32	135.94	55.46	135.94	285.51	57.38
4	18	18.32	135.94	55.46	55.46	116.49	57.38
30	19	18.32	55.46	135.94	135.94	285.51	57.38
17	20	7.48	55.46	55.46	55.46	285.51	140.62
3	21	7.48	135.94	55.46	55.46	116.49	140.62
18	22	18.32	55.46	55.46	55.46	285.51	57.38
43	23	12.90	95.70	95.70	95.70	201.00	0.00
22	24	18.32	55.46	135.94	55.46	285.51	140.62
13	25	7.48	55.46	135.94	135.94	116.49	57.38
21	26	7.48	55.46	135.94	55.46	285.51	57.38
41	27	12.90	95.70	95.70	95.70	0.00	99.00
14	28	18.32	55.46	135.94	135.94	116.49	140.62
34	29	25.80	95.70	95.70	95.70	201.00	99.00
26	30	18.32	55.46	55.46	135.94	285.51	140.62
27	31	7.48	135.94	55.46	135.94	285.51	140.62
53	32	12.90	95.70	95.70	95.70	201.00	99.00
51	33	12.90	95.70	95.70	95.70	201.00	99.00
31	34	7.48	135.94	135.94	135.94	285.51	57.38
23	35	7.48	135.94	135.94	55.46	285.51	140.62
9	36	7.48	55.46	55.46	135.94	116.49	140.62
29	37	7.48	55.46	135.94	135.94	285.51	140.62
50	38	12.90	95.70	95.70	95.70	201.00	99.00
37	39	12.90	95.70	0.00	95.70	201.00	99.00
12	40	18.32	135.94	55.46	135.94	116.49	140.62

15	41	7.48	135.94	135.94	135.94	116.49	140.62
5	42	7.48	55.46	135.94	55.46	116.49	140.62
8	43	18.32	135.94	135.94	55.46	116.49	140.62
20	44	18.32	135.94	55.46	55.46	285.51	140.62
48	45	12.90	95.70	95.70	95.70	201.00	99.00
10	46	18.32	55.46	55.46	135.94	116.49	57.38
19	47	7.48	135.94	55.46	55.46	285.51	57.38
36	48	12.90	191.40	95.70	95.70	201.00	99.00
40	49	12.90	95.70	95.70	191.40	201.00	99.00
52	50	12.90	95.70	95.70	95.70	201.00	99.00
24	51	18.32	135.94	135.94	55.46	285.51	57.38
25	52	7.48	55.46	55.46	135.94	285.51	57.38
16	53	18.32	135.94	135.94	135.94	116.49	57.38

Appendix B. Experiment Results of Sink (Wollastonite Concentrate).

Run Order	**Grade, %**									
	SiO2	**Al2O3**	**Fe2O3**	**MnO**	**MgO**	**CaO**	**Na2O**	**K2O**	**WOL**	**DIOP**
1	60.96	4.69	0.28	0.04	1.64	27.80	1.55	1.68	52.44	9.53
2	60.56	5.10	0.55	0.04	3.54	26.40	1.77	1.79	43.62	20.58
3	61.83	6.73	0.28	0.03	1.61	24.35	2.33	2.35	45.39	9.36
4	62.40	5.89	0.21	0.04	1.10	26.39	2.04	2.10	51.21	6.40
5	58.88	5.04	0.88	0.05	4.88	25.35	1.73	1.68	37.27	28.37
6	61.54	5.05	0.33	0.04	1.91	27.25	1.69	1.80	50.46	11.10
7	58.60	4.66	0.87	0.04	4.85	26.13	1.59	1.56	38.98	28.20
8	62.61	4.89	0.15	0.04	0.71	28.18	1.66	1.81	56.13	4.13
9	61.32	5.79	0.32	0.04	1.89	25.97	1.98	2.01	47.88	10.99
10	61.61	5.39	0.14	0.03	0.64	27.21	1.80	1.92	54.34	3.72
11	61.61	5.56	0.23	0.04	1.34	26.77	1.86	1.97	51.25	7.79
12	61.08	5.92	0.37	0.04	2.28	25.95	2.04	2.06	46.62	13.26
13	61.51	5.39	0.25	0.04	1.39	26.99	1.83	1.91	51.55	8.08
14	53.05	1.88	0.68	0.05	3.06	38.63	0.58	0.66	70.44	17.79
15	60.94	5.99	0.25	0.04	1.34	25.60	2.04	2.05	48.82	7.79
16	61.18	6.31	0.27	0.04	1.59	25.87	2.12	2.12	48.60	9.24
17	59.73	4.89	0.73	0.05	4.39	27.28	1.59	1.62	42.79	25.52
18	60.88	6.18	0.23	0.04	1.33	25.68	2.15	2.11	49.02	7.73
19	57.12	1.95	0.34	0.05	1.40	38.30	0.51	0.63	74.93	8.14
20	61.99	6.00	0.09	0.03	0.26	26.87	2.02	2.07	54.82	1.51
21	57.22	2.75	0.62	0.05	3.96	32.36	0.85	1.00	54.65	23.02
22	59.89	5.32	0.51	0.04	3.25	25.92	1.83	1.84	43.53	18.90
23	59.60	4.51	0.39	0.04	2.25	28.52	1.51	1.58	52.03	13.08
24	61.64	5.47	0.32	0.04	1.92	25.94	1.98	2.01	47.88	10.99
25	60.91	6.22	0.32	0.04	1.89	25.08	2.16	2.14	46.03	10.99
26	61.45	5.98	0.22	0.04	1.13	25.86	2.03	2.10	50.02	6.57
27	61.13	5.80	0.47	0.04	2.97	25.48	2.03	1.99	43.49	17.27
28	60.16	3.99	0.63	0.05	3.99	28.67	1.27	1.37	46.92	23.20
29	62.32	5.81	0.10	0.03	0.32	26.91	2.03	2.04	54.72	1.86
30	61.58	5.82	0.09	0.03	0.23	26.77	1.99	2.01	54.71	1.34
31	61.49	4.32	0.20	0.03	0.66	29.63	1.42	1.53	59.29	3.84
32	61.49	5.72	0.30	0.04	1.79	26.11	1.93	1.99	48.48	10.41
33	61.19	5.60	0.25	0.04	1.46	26.36	1.88	1.96	50.02	8.49
34	59.68	4.54	0.55	0.04	1.95	28.37	1.52	1.65	52.66	11.34
35	60.05	5.70	0.47	0.04	3.02	25.23	1.97	1.98	42.82	17.56
36	61.52	5.75	0.11	0.03	0.36	27.03	1.92	1.94	54.84	2.09
37	61.68	4.77	0.17	0.03	0.69	28.34	1.59	1.72	56.52	4.01
38	61.71	5.33	0.15	0.04	0.71	27.85	1.75	1.87	55.45	4.13
39	62.21	3.80	0.16	0.04	0.65	30.70	1.21	1.31	61.53	3.78
40	59.42	2.14	0.22	0.04	0.91	35.65	0.66	0.78	70.97	5.29
41	61.54	5.84	0.24	0.03	1.36	26.31	1.96	2.03	50.23	7.91

42	61.15	5.99	0.48	0.04	2.89	25.47	2.04	2.03	43.72	16.80
43	60.80	5.48	0.58	0.04	3.59	26.03	1.86	1.85	42.70	20.87
44	61.48	5.38	0.22	0.04	1.17	27.56	1.78	1.89	53.41	6.80
45	61.42	5.62	0.17	0.04	0.91	26.83	1.89	1.97	52.71	5.29
46	62.58	4.71	0.15	0.03	0.71	28.21	1.55	1.69	56.19	4.13
47	58.57	3.60	0.53	0.05	3.44	31.89	1.08	1.26	55.30	20.00
48	57.80	3.46	0.91	0.05	3.55	31.14	1.07	1.20	53.40	20.64
49	62.75	3.59	0.14	0.04	0.49	30.43	1.10	1.31	61.47	2.85
50	61.62	5.28	0.23	0.04	1.30	26.97	1.76	1.89	51.79	7.56
51	59.32	4.90	0.64	0.04	4.17	26.54	1.61	1.63	41.95	24.24
52	61.78	5.19	0.12	0.03	0.56	27.89	1.67	1.81	56.00	3.26
53	57.28	2.79	0.70	0.05	3.94	31.85	0.84	0.98	53.66	22.91

Appendix C. Recovery of Wollastonite to Sink and Diopside to Float.

Run Order	Woll in Sink, %	Diop in Sink, %	Sink Mass, g	Floated Mass, g	Diop Rec. to Float, %	Woll Rec. to Sink, %
1	52.44	9.53	395.28	604.7	87.6	56.8
2	43.62	20.58	613.69	386.3	58.3	73.4
3	45.39	9.36	451.3	548.7	86.1	56.2
4	51.21	6.40	461.85	538.2	90.2	64.8
5	37.27	28.37	859.43	140.6	19.5	87.8
6	50.46	11.10	398.82	601.2	85.4	55.2
7	38.98	28.20	794.7	205.3	26.0	84.9
8	56.13	4.13	344.74	655.3	95.3	53.1
9	47.88	10.99	433.92	566.1	84.3	57.0
10	54.34	3.72	401.45	598.6	95.1	59.8
11	51.25	7.79	421.48	578.5	89.2	59.2
12	46.62	13.26	585.97	414.0	74.4	74.9
13	51.55	8.08	446.26	553.7	88.1	63.1
14	70.44	17.79	94.59	905.4	94.4	18.3
15	48.82	7.79	466.24	533.8	88.0	62.4
16	48.60	9.24	588.19	411.8	82.0	78.4
17	42.79	25.52	681.66	318.3	42.6	80.0
18	49.02	7.73	88.13	911.9	97.8	11.8
19	74.93	8.14	297.34	702.7	92.0	61.1
20	54.82	1.51	407.71	592.3	98.0	61.3
21	54.65	23.02	523.1	476.9	60.2	78.4
22	43.53	18.90	520.42	479.6	67.5	62.1
23	52.03	13.08	675.12	324.9	70.8	96.3
24	47.88	10.99	423.92	576.1	85.1	58.0
25	46.03	10.99	595.00	405.0	78.4	75.1
26	50.02	6.57	469.7	530.3	89.8	64.4
27	43.49	17.27	652.7	347.3	62.8	77.8
28	46.92	23.20	403.7	596.3	69.1	51.9
29	54.72	1.86	394.21	605.8	97.6	59.1
30	54.71	1.34	428.76	571.2	98.1	64.3
31	59.29	3.84	188.73	811.3	97.6	30.7
32	48.48	10.41	455.2	544.8	84.4	60.5
33	50.02	8.49	420.87	579.1	88.2	57.7
34	52.66	11.34	329.15	670.9	87.7	47.5
35	42.82	17.56	650.79	349.2	62.3	76.4
36	54.84	2.09	370.22	629.8	97.4	55.7
37	56.52	4.01	245.12	754.9	96.8	38.0
38	55.45	4.13	397.11	602.9	94.6	60.4
39	61.53	3.78	61.6	938.4	99.2	10.4
40	70.97	5.29	92.6	907.4	98.4	18.0
41	50.23	7.91	403.43	596.6	89.5	55.6
42	43.72	16.80	453.79	546.2	74.8	54.4
43	42.70	20.87	660.03	340.0	54.5	77.3
44	53.41	6.80	392.39	607.6	91.2	57.5

45	52.71	5.29	429.37	570.6	92.5	62.1
46	56.19	4.13	272.61	727.4	96.3	42.0
47	55.30	20.00	303.05	697.0	80.0	46.0
48	53.40	20.64	302.27	697.7	79.4	44.3
49	61.47	2.85	208.88	791.1	98.0	35.2
50	51.79	7.56	390.19	609.8	90.3	55.4
51	41.95	24.24	624.74	375.3	50.0	71.9
52	56.00	3.26	344.42	655.6	96.3	52.9
53	53.66	22.91	243.74	756.3	81.6	35.9

Appendix D. Regression Equations of Wollastonite and Diopside Recoveries.

Wollastonite Recovery to Sink = 177.6 - 7.34 B-400 - 0.373 HT + 0.330 CA-375 - 0.148 CA-250 - 0.253 R855 - 0.576 R845 - 0.0125 B-400*B-400 - 0.00087 HT*HT - 0.00255 CA-375*CA-375 + 0.00037 CA-250*CA-250 - 0.000250 R855*R855 + 0.00229 R845*R845 - 0.0032 B-400*HT + 0.0102 B-400*CA-375 + 0.0135 B-400*CA-250 + 0.02047 B-400*R855 + 0.0143 B-400*R845 + 0.00302 HT*CA-375 - 0.00058 HT*CA-250 + 0.000792 HT*R855 + 0.00161 HT*R845 - 0.00080 CA-375*CA-250 - 0.000305 CA-375*R855 + 0.00016 CA-375*R845 + 0.000531 CA-250*R855 - 0.00222 CA-250*R845 - 0.000282 R855*R845

Diopside Recovery to Float = -165.0 + 6.27 B-400 + 0.945 HT + 0.629 CA-375 + 1.364 CA-250 + 0.469 R855 + 0.552 R845 + 0.0436 B-400*B-400 - 0.00071 HT*HT + 0.00055 CA-375*CA-375 - 0.00332 CA-250*CA-250 - 0.000262 R855*R855 - 0.00088 R845*R845 - 0.0137 B-400*HT - 0.0176 B-400*CA-375 - 0.0201 B-400*CA-250 - 0.01342 B-400*R855 - 0.0024 B-400*R845 - 0.00179 HT*CA-375 - 0.00087 HT*CA-250 - 0.001762 HT*R855 - 0.00139 HT*R845 - 0.00069 CA-375*CA-250 - 0.000104 CA-375*R855 - 0.00354 CA-375*R845 - 0.000787 CA-250*R855 + 0.00010 CA-250*R845 + 0.000745 R855*R845