DETERMINATION OF PARTICLE ADHESION FOR THE DEVELOPMENT OF A SYSTEM FOR SUSTAINABLE MINERAL BENEFICIATION

Bernardo Moreno Baqueiro Sansao, South Dakota School of Mines and Technology, Rapid City, SD

Jon J. Kellar, South Dakota School of Mines and Technology, Rapid City, SD

William M. Cross, South Dakota School of Mines and Technology, Rapid City, SD

Albert Romkes, South Dakota School of Mines and Technology, Rapid City, SD

Karen Schottler, South Dakota School of Mines and Technology, Rapid City, SD

Abstract

The mineral industry uses tremendous amounts of water every year in the processing of ores. Sustainable practices associated with the processing of ores is of critical importance. This investigation evaluates a dry particle separation process based upon adhesive forces. Glass spheres were chosen to represent silicate minerals, the most abundant type of minerals found in mineral deposits. Disks and beads were surface treated with trichloro(octadecyl)silane (TCOD) and n1-(3-trimethoxysilylpropyl) diethylenetriamine (TMPA). A horizontal impact test was designed and tested to calculate the adhesion force between the glass spheres and a glass disk substrate. Impact of the disk/particle puck causes particle removal as tensile forces act on the particles. The tensile detachment force and adhesive force are equal at a critical particle size. The Johnson-Kendall-Roberts theory was used to determine the interfacial energy between the particles and the surface. The average interfacial energy of pure glass, glass treated with TCOD and with TMPA were 48.53 mJ/m^2, 21.57 mJ/m^2, and 40.08 mJ/m^2, respectively. These values are in good agreement with the literature values. The van Oss-Good-Chaudhuri method was applied to measure the surface energy of microcline and quartz in order to evaluate the results of the glass tests using the impact method. Impact tests using those same minerals as particles were also performed however, the irregularity of the mineral particles is one of the challenges to accurately measure the interfacial energy through the impact test method.

Introduction

The mineral industry requires tremendous amounts of water to separate valuable minerals from ores. Flotation is a common process to separate minerals being conducted at approximately 25 to 40 wt% solids [1]. A conventional comminution-classification-flotation circuit to process copper sulfide ore is an example of required water in the treatment of minerals, ranging from 1.5 to 3.5 m^3 of water per metric ton of ore processed [2]. As most of the copper mines in the United States are located in the desert southwest (Arizona and New Mexico), therefore a sustainable practice associated with the processing of ores is of critical importance to reduce the amount of water necessary to keep plants operating, and also to make it feasible to start and develop new operations in desert areas.

Exploitation of differences in adhesive forces between particles and a flat substrate is one additional potential gateway to develop a dry, sustainable process for mineral separation and concentration. Measurements of adhesive forces can be accomplished through various techniques [3-5] and are often considered somewhat tedious and time consuming. Regardless of these challenges, it is important to understand how the surface energy of solids contributes to the adhesion of particles to a substrate, and this was the focus of this research.

In 1971, Johnson, Kendall and Roberts (JKR) developed a model that includes the effect of adhesion force on the deformation of an elastic sphere in contact to an elastic half space [6]. The JKR theory is an adhesion energy theory that infers that the pressure distribution at contact is such that all short-range contact forces exist within the contact area adding an adhesion force to the classical Hertzian [7] contact theory. However, when using a solid with high elastic modulus (glass in this case), the deformation produced by the attractive forces is very small [6], thus the deformations can be neglected. Zafar et al. [3] built upon the JKR theory to develop a drop test method for the determination of particle adhesion (interfacial energy). In this research the Zafar method was adapted to measure interfacial energy in what is referred to here as a *'mechanical approach'*.

Surface treatments with hydrophobic and hydrophilic chemicals were performed to alter the surface properties of the solids. Solids can have their natural relation with water changed by coating the surface with a certain type of chemical. Glass is naturally hydrophilic, i.e. a drop of water spreads completely over the glass surface. But when coated with a silane the water interacts differently and it does not spread over the glass surface.

The van Oss-Good-Chaudhuri method (VOGC) [8] has been used in this work to measure the surface energy of quartz and microcline. This method includes the Lifshitz-van der Waals, Lewis acid and Lewis base interactions between solid and liquid. A triad of three liquids with known surface tension components is used in order to calculate the solid's surface energy. To find the Lifshitz-van der Waals component, a non-polar liquid is used (e.g. diiodomethane (CH_2I_2)). Also needed are a liquid that is heavily dominant Lewis acid (e.g. water) and one that is highly Lewis basic (e.g. ethylene glycol ($C_2H_6O_2$) or glycerol ($C_3H_8O_3$)).

The surface energy can be used to determine the adhesion between two solids [4]. The most accurate calculation of surface energy comes from using the advancing angle of the contact angle hysteresis [9].

When the surface with the adhering drop is tilted, advancing (down-hill) and receding (up-hill) angles form. The advancing angle is the angle measured just before the liquid begins to slide and is the instance of strongest adhesion for that solid [9]. Thus, using the advancing angles in the VOGC method (*'molecular approach'*) yields solid surface energy values that represent the lowest energy regions of the surface [10].

Materials and Methods

For the determination of particle adhesion, the interfacial energy was measured and calculated based on an impact test first develop by Zafar et al. [3] and adapted for the needs of this research. In this investigation, micron size glass spheres (-100 μm +10 μm and density of 2.48 g/cm^3) were chosen to represent silicate minerals, the most abundant type of mineral found in mineral deposits [11], and to work as model particles. Figure 1 shows a micrograph of the beads used in the experiments.

The beads were poured onto disks of 8 mm in diameter, purchased from Electron Microscopy Sciences. The interaction between the particles and substrate (disks) were tested with three different surface treatments, these being: plasma cleaned using a Harrick Plasma Cleaner, where the disks were treated for at least 5 minutes on each side; treated with trichloro(octadecyl)silane (TCOD) after plasma cleaning; and, treated with n1-(3-trimethoxysilylpropyl) diethylenetriamine (TMPA) after plasma cleaning. See Figure 2 for the structure of these molecules. Both chemicals were supplied by Sigma-Aldrich®. Before each treatment all the disks and beads were plasma cleaned to avoid any organic material to contaminate any surface.

The treatment with TCOD was performed in a solution of 1.5 ml of this substance and 40 ml of toluene for each 2 grams of glass used. Beads and disks were treated in different containers. The glass particles were agitated in solution for 2 hours and then cured (dried) for 2 hours at 150^{o}C.

TMPA was used as a 5% v/v solution in absolute methanol, with 100 ml of solution for every 4 grams of glass prepared. The same solution contact time and curing time were applied in this treatment as was used in the hydrophobic treatment.

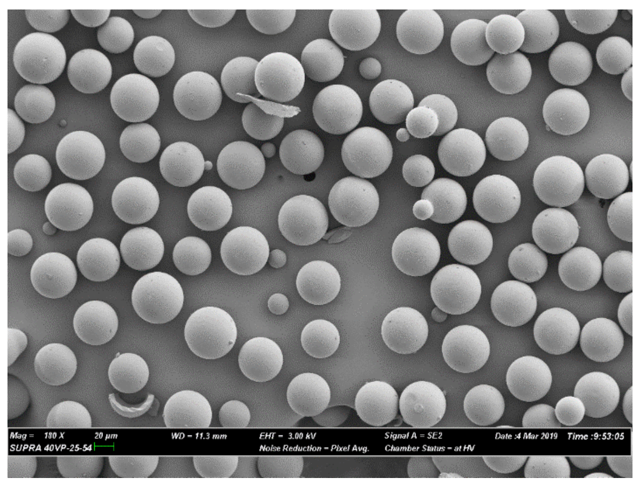
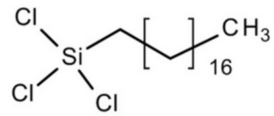
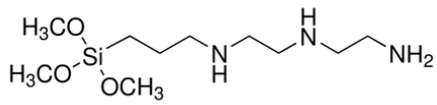


Figure 1. SEM micrograph of glass beads



Trichloro(octadecyl)silane



n1-(3-trimethoxysilylpropyl) diethylenetriamine

Figure 2. Molecular structures of TCOD and TMPA

Glass disks were glued on an aluminum stub of about 15 mm in diameter and 25 mm in length. The beads were then sprinkled over the disk, yielding a single layer of beads covering most of the disk area; an example of this is shown in Figure 4. In order to measure the interfacial velocity, a portable device, was designed and fabricated. A horizontal tube with maximum length of 50 cm, was mounted on an aluminum base supported by aluminum columns (providing enough weight to hold the system in place during the tests – shown in Figure 3). An aluminum backstop with an opening of 12 mm was placed at the end of the glass tube. The aluminum stub was then propelled using an air compressor with a pressure regulator, adjusting the pressure to achieve the desired velocity. The stub accelerated and impacted on the backstop against the opening at the end of the tube. The velocity and duration of impact was measured using a high-speed camera (IDT MotionProY Series 4), recording every impact at a rate of 70,000 frames per second. The impact provoked a tensile force between particle and surface because of the sudden stub deceleration.

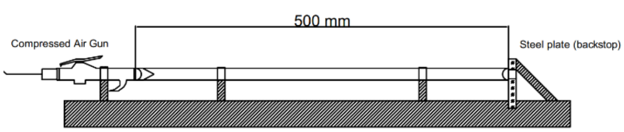


Figure 3. Schematic representation of the impact test equipment.

The adhesion force between two bodies is obtained by following the same application of the JKR theory used by Zafar et al. [3], which uses Equation (1), where F_{ad} is the JKR [6] adhesive force, Γ is the interface energy and R is the particle radius. The detachment force of a particle due to momentum is obtained from Equation (2), where F_{det} is the detachment force, m is the mass of the particle, Δt is half of the time of impact (i.e. half of the time of contact between stub and backstop) and v is the impact velocity. The interface energy was then estimated from Equation (3), where $F_{det} = F_{ad}$.

$$F_{ad} = \frac{3}{2}\pi R\Gamma \quad (1)$$

$$F_{det} = \frac{m\Delta v}{\Delta t} \quad (2)$$

$$\Gamma = \frac{m\Delta v}{\Delta t \pi R}\frac{2}{3} \quad (3)$$

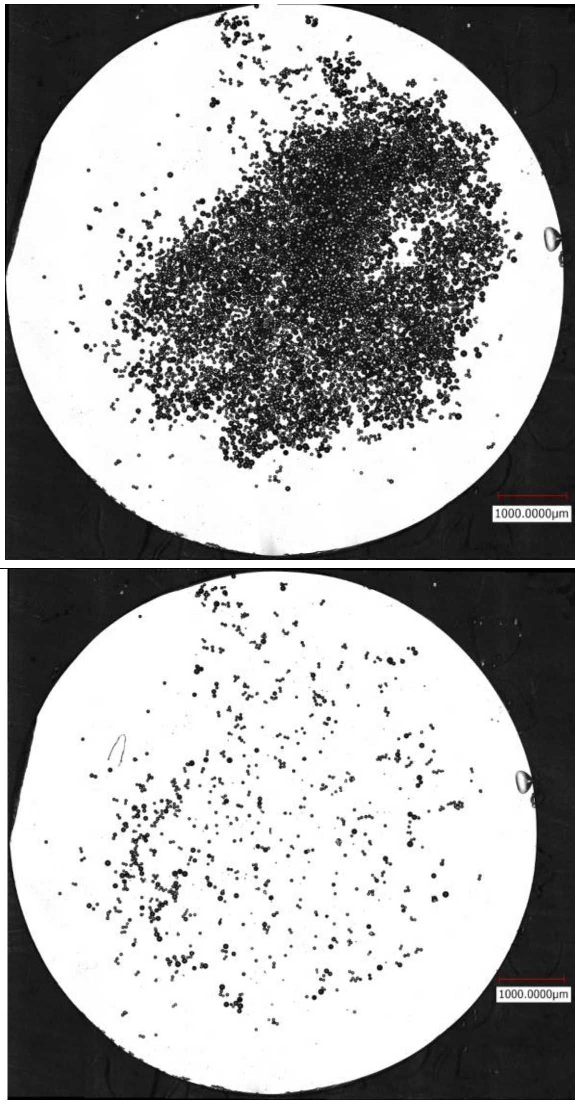
Whenever the adhesive force is greater than the detachment force ($F_{ad} > F_{det}$), particles will remain attached on the disk surface for a given particle size. There is a critical particle size at which $F_{ad} = F_{det}$. This critical size indicates that particles will detach if they are bigger than the critical size and particles will remain attached if they are smaller than the critical size [3]. An image of the beads on the surface of the disk was taken before (see Figure 4a) and after (see Figure 4b) each test using a laser profilometer (Keyence VK 200X). The image of the disk after the test was then analyzed using ImageJ software to determine the size of the beads that remain attached to the disk. The largest size left on the disk was used to calculate the adhesion energy of the particles.

To determine the surface energy of quartz and microcline, the VOGC method was applied. For the measurement of contact angle between the liquids elected for this investigation, and the glass slides, a Ramé-Hart Model 500 Goniometer/Tensiometer was used. The selected liquids for the series of tests were: distilled water (H_2O, noted as W), ethylene glycol ($C_2H_6O_2$, noted as E), glycerol ($C_3H_8O_3$, noted as G), diiodomethane (CH_2I_2, noted as D). The surface energy of a given solid material is calculated solving simultaneously a system of three equations and three unknowns. Equation (4) shows the equation that is used to calculate:

$$\gamma_{LiG}(1+\cos\theta_i) = 2(\gamma_{LiG}^{LW}\gamma_{SG}^{LW})^{0.5} + 2(\gamma_{LiG}^{a}\gamma_{SG}^{b})^{0.5} + 2(\gamma_{LiG}^{b}\gamma_{SG}^{a})^{0.5} \quad (4)$$

Where γ is the surface free energy (mJ/m^2), LiG is the liquid-gas component for each liquid, i, SG is the solid-gas component, LW indicates the Lifshitz-van der Waals component (mJ/m^2), a indicates the Lewis acid component (mJ/m^2), b indicates the Lewis base component (mJ/m^2), θi is the contact angle between liquid i and the solid (in degrees).

Classroom mineral specimens of microcline and milky quartz were purchased from Ward's Science. Each mineral was crushed (jaw and roll crushers). The microcline was then dry sieved for 10 minutes. The quartz sample was ground in a laboratory ball mill for 15 minutes and wet sieved for 10 minutes. The -45 µm +38 µm size fraction of each mineral was plasma cleaned and used in the impact test.



a
b

Figure 4. Plasma-cleaned glass disk with glass beads a) before and b) after impact.

A specimen of microcline and a specimen of quartz were used to measure the contact angle using three liquids through the VOGC method. The surface of microcline was polished to provide a flat surface, whereas a face of a quartz crystal was used to perform the contact angle measurements.

Results and Discussion

The tests of impact were carried out under the same pressure of 2.50 psi, for comparation purposes, to keep the same velocity of impact in all the tests (with little variation). The room temperature was between 20ºC and 25ºC and relative air humidity between 32% and 53%. The tests were performed on the same day of the plasma cleaning and the chemical treatment to avoid contamination from air particles during storage of the materials. The velocity of impact and time of contact between the stub and stopper is recorded using the high-speed camera. The size of the beads that remained attached was measured using ImageJ. The interfacial energy was calculated using Equation 3.

Tests with plasma cleaned glass

These tests were carried out using glass with no chemical treatment, only with plasma cleaning to remove organic matter that could be present on the disk and the beads. Table 1 below shows the results of the tests.

Table 1. Results of the tests with plasma cleaned beads and disks

Trial #	Glass Disk Treat.	Bead Treat. Type	Critical Radius of Particles (m)	Impact Velocity (m/s)	Interfacial Energy (mJ/m^2)
1	Plasma Cleaned	Plasma Cleaned	4.48E-05	1.72	46.29
2			4.35E-05	1.72	59.19
3			4.63E-05	1.75	64.54
5			4.78E-05	1.59	53.36
7			4.20E-05	1.42	28.63
8			4.66E-05	1.58	39.14
Average			4.52E-05		48.53

The critical radius of the particles varied little from 42.0 µm to 47.8 µm (diameters of 84.0 and 95.6 µm, respectively). Using Equation 3, the interfacial energy varied from 28.63 mJ/m^2, in the Stub 7 trial, to 64.54 mJ/m^2 in the Stub 3 trial. An average of 48.53 mJ/m^2 and 45.2 µm were recorded for the interfacial energy and the critical radius of particles , respectively. This average value of 48.53 mJ/m^2 is in very good agreement with the literature critical surface tension value of 47 mJ/m^2 [12]. Figure 4 shows the images before (4a) and after (4b) the impact for plasma cleaned treatment. Figure 5 shows the relationship between the impact velocity and the interfacial energy, where a behavior of increasing interfacial energy with increasing impact velocity can be seen. Asperities and roughness on the surface of the substrate and the beads could interfere in the results, minimizing the contact area and overestimating the interfacial energy [13].

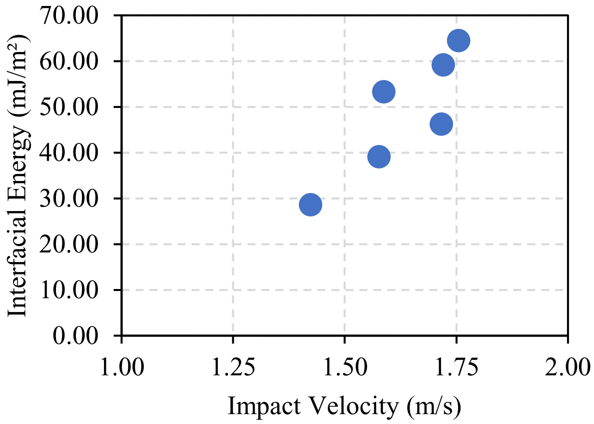


Figure 5. Interfacial energy as a function of impact velocity – Plasma cleaned disk and beads.

Tests with TCOD treated glass

These tests were performed using TCOD to treat the glass after plasma cleaning. Table 2 below shows the results of the tests. The interfacial energy varied from 17.22 mJ/m^2 to 26.82 mJ/m^2, with an average of 21.57 mJ/m^2. The average critical radius was $2.69x10^{-5}$ m (diameter of 53.8 µm), being it smaller than the critical radius of the plasma cleaned glass. Being a hydrophobic chemical, the results of the impact tests indicate what is expected, that the TCOD treatment decreases the interfacial energy of the solid. The average value of 21.57 mJ/m^2 also agrees with the literature value for this same type of treatment ranging between 20-24 mJ/m^2 [12]. The decrease of the average critical radius is another indication that the interaction between the particles and the substrate has changed. Figure 6b shows that far fewer beads remained attached to the disk after the impact. Figure 8 shows the relation between interfacial energy and impact velocity for these tests.

Table 2. Results of the tests with TCOD treated beads and disks

Trial #	Glass Disk Treatment	Bead Treat. Type	Critical Radius of Particles (m)	Impact Velocity (m/s)	Interfacial Energy (mJ/m^2)
1	TCOD	TCOD	3.09E-05	1.72	26.82
2			2.49E-05	1.80	17.22
5			2.66E-05	1.76	20.27
12			2.53E-05	1.78	21.98
Average			2.69E-05		21.57

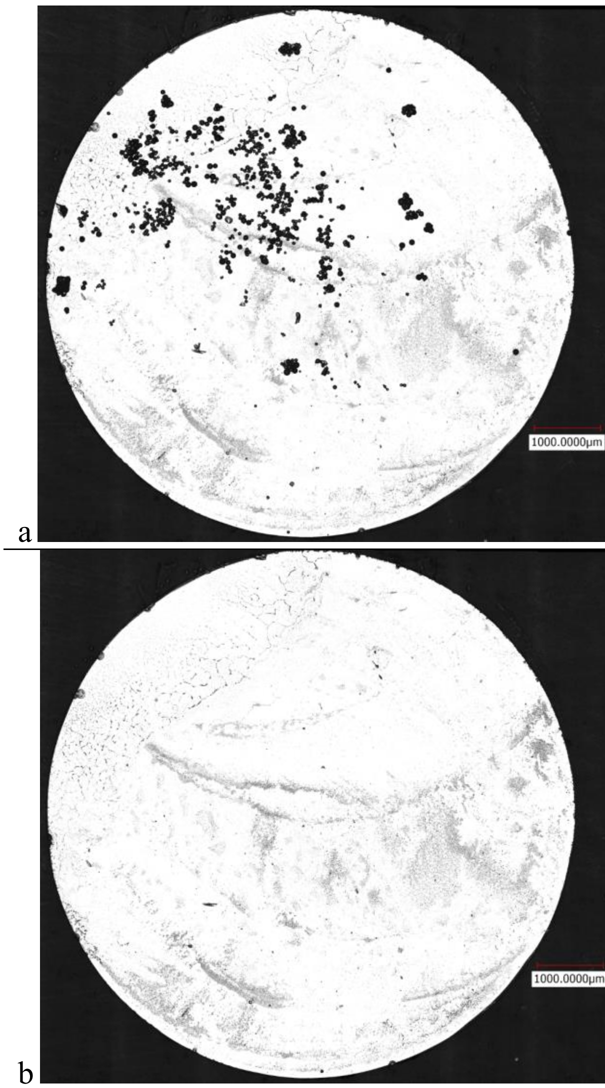


Figure 6. TCOD tread glass disk and TCOD treated beads a) before and b) after impact.

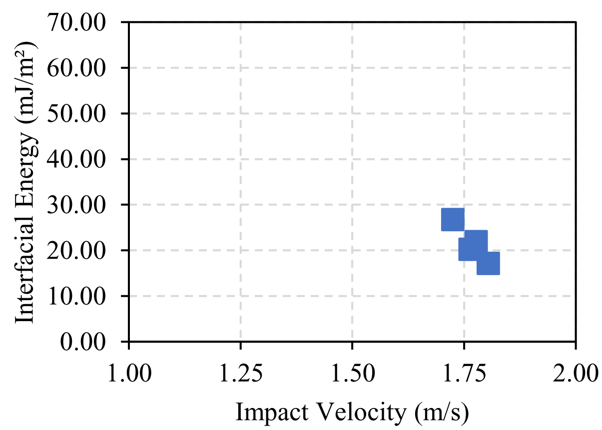


Figure 7. Interfacial energy as a function of impact velocity – TCOD treated disk and beads.

Tests with TMPA treated glass

Next, tests were performed using TMPA to treat the glass after plasma cleaning. Table 3 below shows the results of the tests. The average critical radius was 4.59×10^{-5} m (diameter of 91.8 µm), similar the critical radius of the plasma cleaned glass and greater than the critical radius of the TCOD treated tests. The interfacial energy, from 35.83 $mJ/m^2 /m^2$ to 47.24 $mJ/m^2 /m^2$, with an average of 40.08 $mJ/m^2 /m^2$. Since TMPA is a hydrophilic chemical, it is expected that the interfacial energy is going to be greater than the TCOD treatment, but smaller than pure glass. The literature value of the surface tension for this chemical treatment is 37.5 $mJ/m^2 /m^2$ [15]. The average of 40.08 $mJ/m^2 /m^2$ is in the same order of magnitude and closer to the literature value. Also, as expected, Figure 8 shows more beads than TCOD treatment but less beads than plasma cleaned glass treatment in the picture after the impact.

Table 3. Results of the tests with TMPA treated beads and disks

Trial #	Glass Disk Treatment	Bead Treat. Type	Critical Radius of Particles (m)	Impact Velocity (m/s)	Interfacial Energy ($mJ/m^2 /m^2$)
1	TMPA	TMPA	5.11E-05	1.70	47.24
6			4.94E-05	1.62	35.83
9			4.16E-05	1.47	41.34
12			4.15E-05	1.75	35.91
Average			4.59E-05		40.08

Figure 9 shows a different behavior than the ones previously discussed (for plasma cleaned and TCOD treatment) in that there is not a significant change in the interfacial energy when the velocity increases, as the interfacial energy value unchanging with different velocities.

Tests with microcline

The same procedure described in the section *Tests with plasma cleaned glass* was repeated using ground microcline (-45 µm +38 µm) instead of spherical beads. Due to the irregularity of the ground mineral, it cannot be stated that there is a known area of contact between the particle and the substrate. Because of this irregularity, the mineral particles did not have a defined contact area with the substrate and the majority of the particles did not remain attached after the impact. Figure 10 shows the particles on the substrate before (Figure 10a) and after (Figure 10b) the impact. However, because the mineral was dry sieved, submicron size particles that were agglomerated with the larger particles remained attached after the impact. The interfacial energy was not accounted for this case.

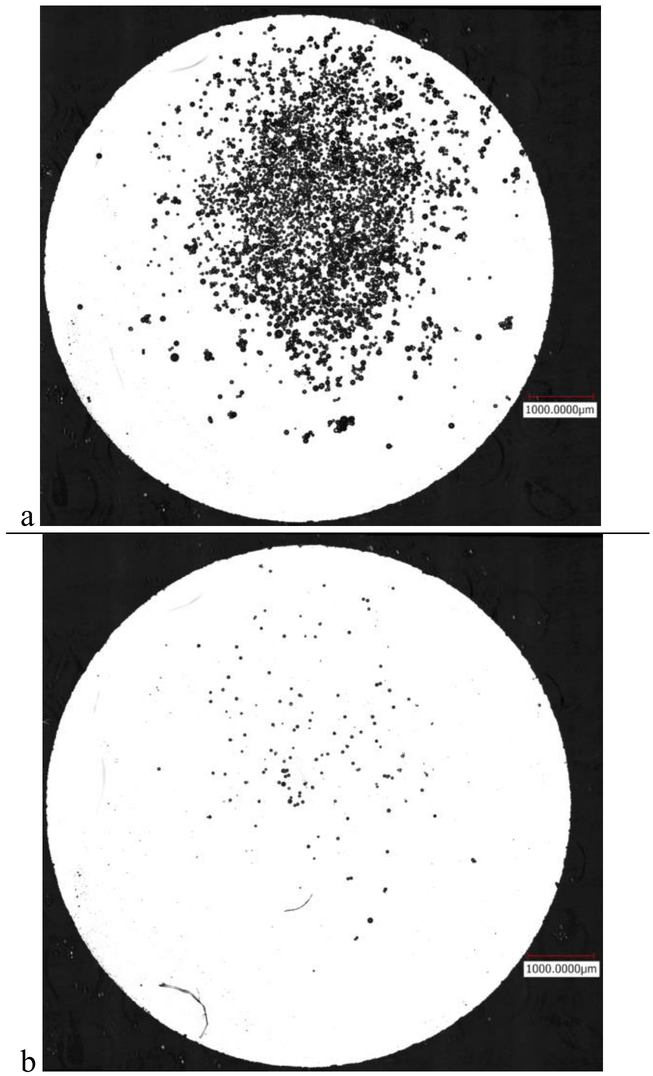


Figure 8. TMPA tread glass disk and TMPA treated beads a) before and b) after impact.

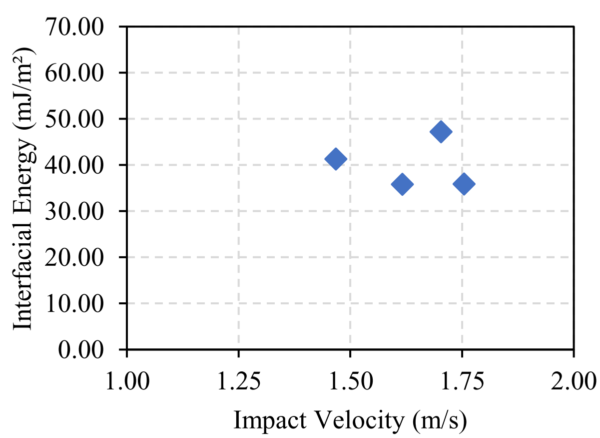


Figure 9. Interfacial energy as a function of impact velocity – TMPA treated disk and beads.

Tests with quartz

Once again, the procedure described in the section *Tests with plasma cleaned glass* was followed for the quartz (-45 µm +38 µm) impact tests. Since the ground sample was wet sieved, it did not have the same agglomerated submicron size particles among the larger particles as it happened at the microcline tests. A different behavior can be seen in Figure 11. Quartz particles did remain attached after the impact. With no interference of tiny particles, the contact area between the larger quartz particles and the substrate was higher and the interaction was then stronger.

For the calculation of the interfacial energy, the area of the particles was measured using ImageJ. The radius of the particle was considered to be the radius of a circle of same area. Table 4 shows the results of the impact tests.

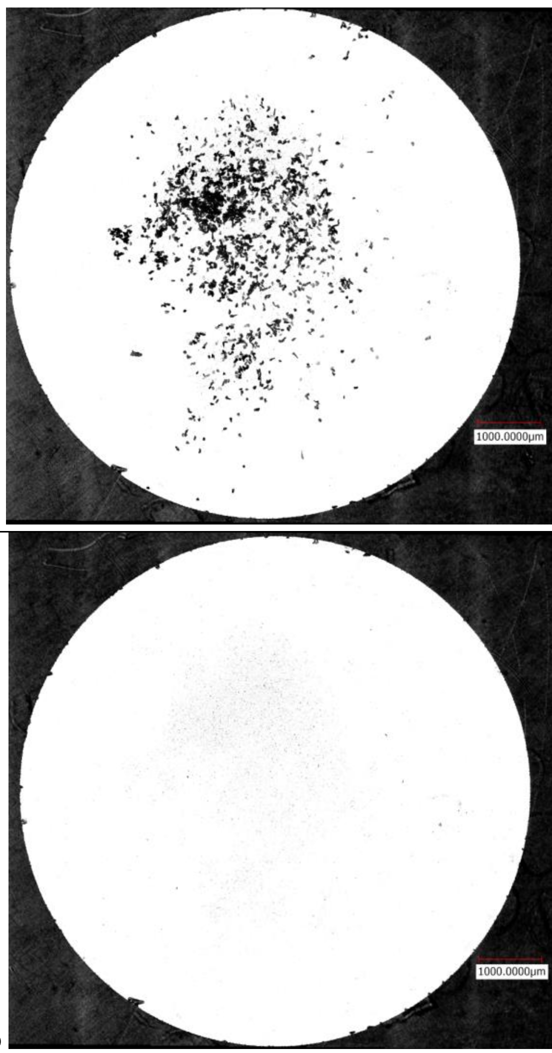


Figure 10. Plasma cleaned glass disk and plasma cleaned microcline a) before and b) after impact.

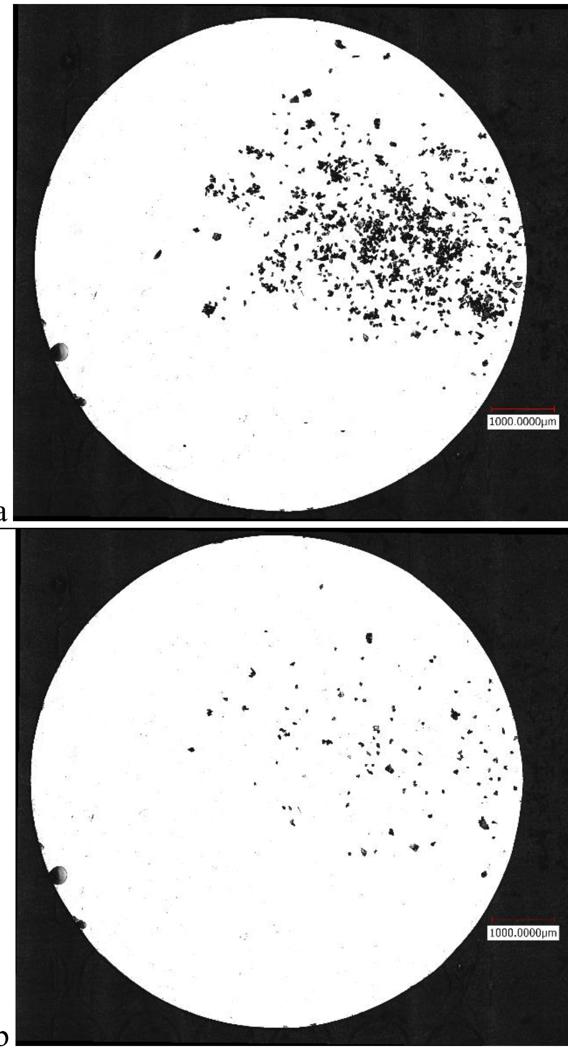


Figure 11. Plasma cleaned glass disk and plasma cleaned quartz a) before and b) after impact.

Table 4. Results of the tests with plasma cleaned quartz and disks

Trial #	Glass Disk Treatment	Mineral	Critical Radius of Particles (m)	Impact Velocity (m/s)	Interfacial Energy (mJ/m^2)
2	Plasma Cleaned	Quartz	7.73E-05	1.27	95.91
4			7.49E-05	1.28	102.61
5			7.15E-05	1.18	79.50
Average			7.46E-05		92.68

Contact angle tests

Table 5 shows the results of the surface energy of the minerals using the VOGC method. It can be seen that the calculated surface energy of the minerals is in good agreement with the interfacial energy measured for the plasma cleaned glass using the impact test method.

Table 5. Surface Energy (mJ/m^2) for different minerals

Substrate	Liquid Triads		
	W-D-E	W-D-G	W-D-S
Microcline	47.1 ± 1.3	64.3 ± 1.0	48.7 ± 2.7
Microcline Advancing	45.9 ± 1.3	63.4 ± 1.0	45.1 ± 2.7
Quartz Crystal	47.0 ± 0.6	57.7 ± 0.1	50.9 ± 1.6
Quartz Crystal Advancing	48.4 ± 0.6	54.9 ± 0.1	44.4 ± 1.6

However, the interfacial energy of the quartz mineral measured using the impact test is about the double of the surface energy measured using the VOGC method. This difference is most likely due to the contact area between the quartz particles and the disk which can be greater than the contact area between beads and substrate, increasing interfacial energy between the mineral and substrate.

Conclusions

The impact test apparatus is a good method to measure the interfacial energy between solids. This method is the first step to develop a sustainable system that does not use water to separate and concentrate minerals. The values measured in the experiments are in good agreement with literature values of critical surface tension. The average interfacial energy (and literature values) of pure glass, glass treated with TCOD and with TMPA were 48.53 mJ/m^2 (47 mJ/m^2), 21.57 mJ/m^2 (20-24 mJ/m^2), and 40.08 mJ/m^2 (37.5 mJ/m^2), respectively. The use ground of minerals to determine the surface energy applying the impact test method is challenging mainly due to the irregularity of the ground particles. Exploratory tests have revealed that there is adhesion between irregular particles and a substrate. The data will be integrated with computer simulation program to predict ideal mineral separation conditions and design a plant scale equipment to make dry separation feasible for new and existent plant operations.

Acknowledgements

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