

Selective Flotation of Zinc and Lead from Sphalerite and Galena – Exploring Ecologically Sustainable and Economical Reagents

Steven Kuba Nuhu^{a,*}, Hamoud Alenezi^b

^aDepartment of Minerals and Petroleum Resources Engineering, School of Engineering, Plateau State Polytechnic, Barkin-Ladi, Nigeria

^bDepartment of Chemical Engineering, The Public Authority for Applied Education and Training, College of Technological Studies, Kuwait
 kubsteven3@gmail.com

Sodium cyanide (NaCN) and sodium sulphide (Na₂S) are frequently employed in selective flotation to depress Lead (Pb) in galena during the froth flotation of sphalerite/galena (ZnS/PbS). Due to their extreme toxicity, there is now more emphasis on developing environmentally and economically sustainable alternative reagents. Following crushing and grinding of the Zurak-Wase ZnS/PbS, was sieve analysis, which yielded a range of -0.71+0.50 particle size and a 50 % cumulative weight passing for optimum liberation. The ZnS/PbS was separately floated in a Denver flotation cell in the presence of 2, 4 and 6 g of corn starch (CS). This produced concentrates of 189 g, 219 g, and 235 g with the corresponding tailings of 110 g, 81 g, and 65 g. The XRF analysis shows 499,997 ppm Pb was best activated and depressed 294,933 ppm Zn with 6 g of CS. It is noticed that CS is a promising Pb activator and Zn depressant with an increased volume which improves the material hydrophobicity and hydrophilicity in that order. CS at higher volume can be used to selectively float Pb from Zn when Pb is a material of the target. CS has proved to be a replacement for NaCN and Na₂S to mitigate the ecological challenges related to them. Also, it is an effective reagent to selectively activate Pb and depress Zn. Alternative organic materials like dextrin, citric acid, and tannins should be investigated to selectively depress Zn or activate Pb.

1. Introduction

The mining and minerals processing industries hold a pivotal role in the global economy as they provide essential raw materials for various industrial sectors. Among the minerals extracted from the Earth's crust, zinc (Zn) and lead (Pb) have gained significant attention and are two vital constituents found in ore deposits worldwide (Yu et al., 2017). Zn in sphalerite (ZnS) and Pb in galena (PbS) often coexist in deposits and have grown in importance due to their applications in the metallurgical industry (Pashkevich et al., 2023). Zn is known for its anti-corrosive properties which serve as an electroplating substance and an alloying agent (Ge et al., 2015). Lead, indispensable in batteries, radiation shielding, electronics, cable sheathing, and galvanization, contributes significantly to the economic landscape (Khosro et al., 2019). Due to the economic significance among other minerals, sphalerite and galena deposits have spurred extensive research efforts aimed at selectively optimizing their separation (Wang et al., 2022).

Selective flotation methods have become the cornerstone of mineral separation (Hao et al., 2018). Due to the coexistence of the ZnS and PbS, normal froth flotation finds it difficult to separate them, as a result of this, selective flotation may enhance their separation and concentrations (Cheng et al., 2023). Froth flotation relies on physicochemical differences between minerals, including their surface properties and affinity (hydrophobicity and hydrophilicity) with reagents such as collectors, frothers, depressants, and modifiers Rasib et al., (2023). Traditionally, sodium cyanide (NaCN) and sodium sulphide (Na₂S) have been used to selectively depress or activate sulphide minerals such as ZnS and PbS during the flotation of complex ores like copper (Cu), Zn and Pb (Han et al., 2020). Sodium cyanide and sodium sulphide could also induce coagulation of fine ZnS particles,

and such thickening significantly reduced the mechanical entrainment of the fine ZnS (Nanda et al., 2023). It was then noticed that large volumes of NaCN and Na₂S may have to be used for the effectiveness of selectively depressing ZnS by making the mineral surface hydrophilic (Khosro et al., 2019). NaCN and Na₂S are highly toxic compounds, and can potentially leach into water bodies, leading to contamination of aquatic ecosystems (Saim and Darteh, 2023).

In froth flotation, starches from various agricultural products have reportedly been used as either depressants or activators for certain minerals (Yan et al., 2020). The substances in starches responsible for these effects are primarily polysaccharides (Mondal et al., 2021). In Brazil, cassava starch has also been widely used as a depressant in the inverse flotation of quartz, and depressing iron ore (Li et al., 2018). The starch market has been growing and improving in recent years (Alenezi and Al-Qabandi, 2022), leading to better products attending to the requirements of the mineral industry (Liu et al., 2020). Achieving the desired selectivity by starches from different farmed produce on minerals has long been a subject of research interest.

As a result of environmental pollution and the difficulty with which selective separation is achieved, this paper is aimed at exploring alternative and environmentally friendly reagents, and economically competitive for selective froth flotation to mitigate the environmental concerns caused by NaCN and Na₂S. In this study, corn starch (CS) was employed on a sample of ZnS/PbS where the hydroxyl groups in the starch amylose and amylopectin interacted with mineral surfaces through hydrogen bonding and adsorption which are responsible for depression or activation. The characterisation of the floated samples is to be conducted and highlight the performance of CS selectivity, and recovery.

2. Methodology

The materials and equipment used include Sphalerite/Galena, Denver D-1 Lab Flotation Cell, Savona Equipment Ltd., British Columbia, Canada. Laboratory DIN4188 tests sieves and sieve shakers, Endocotts Ltd., London, United Kingdom. TMAX-LBM-LS laboratory roll ball mill, Xiamen Tmax Battery Equipment Limited, Fujian Province, China. Benchtop pH meter, WINCOM Company Ltd., Jiangsu, China. SET1414 Laboratory Jaw Crusher, SE-Test Lab Instruments (I) Pvt. Ltd., Delhi, India. Laboratory ZPW-4 Pulveriser, Lantytto® Machines Ltd., Shanghai, China. 911MPE-TM-LCC21 Laboratory Cone Crusher, 911 Metallurgy Corp., Langley, British Columbia, Canada. Lime from Graymont Ltd, Pittsburgh, Pennsylvania, USA. 99 % pure Oleic acid, Alpha Chemika, Mumbai, India. DOV-55S Vacuum Laboratory Oven, Infitek Company Ltd., Shandong, China. Others are Corn starch, kerosene, digger, shovel, and water.

The square sample collection method was adopted where an area of 4 km² was labelled A, B, C, D, E, F, G, H, and I. All the sphalerite/galena samples were dug with the use of a digger and shovel.

The sample was grounded with a primary jaw crusher, and the average size of the particle was reduced from 50 mm to 10 mm. A cone crusher (secondary crusher) reduced it to a particle size of 5 mm. Subsequently, a roll crusher (tertiary crusher) further reduced it to a size of 2 mm. A pulverization machine milled it to -2 mm.

The sieve analysis was conducted on the pulverised products. A 300 g of the material was separated into various particle sizes through eleven (11) stacked sieves arranged in series, starting with a sieve of 1.4 mm, and progressing to smaller sieve openings. Subsequently, the stacked sieves were shaken for 30 min on a sieve shaker. Particles larger than each sieve opening were retained while allowing smaller particles to pass through each sieve. The cumulative percentage of particles retained and passed through each sieve was calculated, and a graph was plotted to determine the particle size distribution and optimum size for mineral grain liberation. A 300 g sample of sphalerite/galena optimum particle size obtained from the sieve analysis was mixed with 1 litre of water in the flotation cell and agitated for 4 min to achieve homogeneity. Following this, two drops of lime (calcium sulphate – a pH regulator) were added to the sphalerite/galena pulp and vigorously stirred for 3 min to stabilize the pH, initially set at 10.5. Subsequently, two drops of oleic acid (collector) were introduced to the pulp and conditioned for 4 min. Then, 2 g of CS was added and conditioned for another 4 min. Finally, 2 drops of kerosene (frother) were added to the pulp and conditioned for 3 min to facilitate froth formation. The air was induced into the pulp by turning the knob on the stem of the Denver flotation cell. The resulting froth was continuously skimmed off into a clean dry container and collected the concentrate until no froth was no more formed. Subsequently, the same process was followed using 4 g and 6 g of CS under the same flotation conditions. The concentrates and the tailings were separately dried using a laboratory oven set at 40 °C for 3 d. The fine powdered mineral ores and the tailings from the flotation processes were used for the characterization. The prepared samples (concentrate and tailings) were separately placed in the XRF machine and irradiated with X-rays generated by an X-ray tube, where the atoms in the sample were excited. As these atoms returned to their ground state, they emitted secondary (fluorescent) X-rays with characteristic energies or wavelengths and intensities which identified and evaluated the elemental composition of each element.

3. Results and Discussion

3.1 Zurak-Wase Sphalerite/Galena

The sphalerite/galena sample was obtained from Zurak, Wase Local Government Area, Nigeria. Zurak is located southeast of Jos, the Plateau State capital within 216 km. It is located within longitudes 0958'00"E; 1038'00"E and latitudes 0859'00" N; 0921'00" N. Zurak receives a yearly average temperature of 26.5 °C, 1,941 mm rainfall, and 23 % relative humidity. Its climate is Guinea Savannah (Ramli et al., 2023).

3.2 Sieve Analysis for Particle Size Distribution

The cumulative weight passed and retained during the sieve analysis is shown in Figure 1. The intersection point on the graph shows a particle size range between $-0.71+0.50$. This indicates that particles in the size range of $-0.71+0.50$ mm make up 50 % of the Zurak-Wase sphalerite/galena sample. This demonstrates the ideal particle size to release lead and zinc during flotation as effectively as possible. Additionally, because it enables better separation of the important minerals (sphalerite and galena) from the gangue material, it guarantees that particles in this size range are necessary for optimizing the flotation process' efficiency. Lower recovery rates can occur from too-large particles that may not completely liberate the targeted minerals. In contrast, too fine particles can cause problems such as handling, processing, and increased reagent usage. Mineral processing companies can maximize the efficiency and effectiveness of the flotation process by determining the range of particle sizes in which 50 % of the sample falls. This can be done by optimizing grinding and milling processes to meet this aim. As a result of the more exact and effective use of resources, this optimizes lead and zinc recovery rates, lowers processing costs, and lessens the environmental impact. According to Tan and Choi, (2023), sieve analysis is a fundamental technique that provides a profound understanding of particle size distributions and characteristics. Liu et al., (2019) reiterated that, by precisely determining particle size ranges, the mineral industries can process and maintain optimal consistency in mineral liberation at a reasonable cost.

Researchers utilize sieve data to study the behaviour of materials under different conditions, explore new processing techniques, and develop innovative products with tailored properties and functionalities. In essence, sieve analysis serves as a versatile tool that empowers industries to make informed decisions, optimize processes, ensure product quality, and drive innovation in mineral processing and beyond.

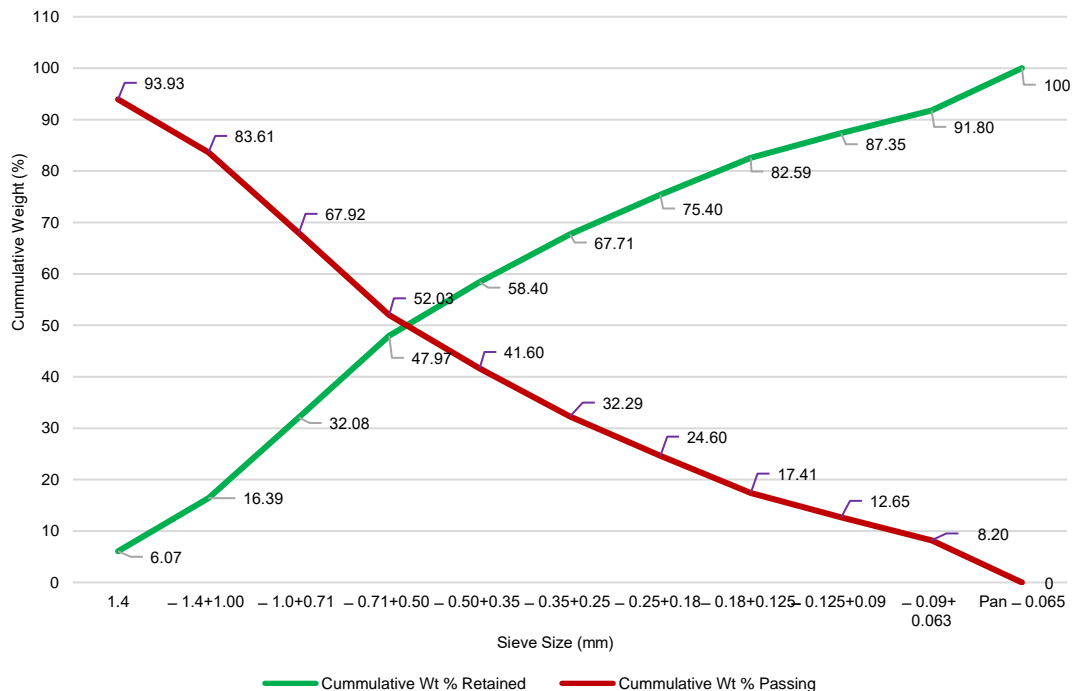


Figure 1: Sieve Analysis of Zurak Sphalerite/Galena Ore

3.3 Flotation of Sphalerite/Galena

The flotation of sphalerite/galena by the reagent of CS shows the concentrate and tailings in Table 1. The results indicate that more concentrates were recovered as more concentration of CS was used. It is noted that the initial

300 g of material was not entirely recovered from the flotation process using 2 g of CS. There are several reasons for this disparity, such as when material is partially transferred from one container to another at different stages of the processes, spills or losses may occur. Some materials can attach to the machine and not get completely recovered in the concentrate or tailings. Discrepancies may arise from measurement errors made at either the beginning or end of the weighing process. Weighing scale calibration errors can result in small variations in the weights that are measured. Others include small variations that may result from inaccurate weight capturing or overlooking decimals that are capable of rounding up. There is a chance that some tiny particles will either stay in the filter media or go past the process filters. A portion of the material could alter chemically during flotation, producing gas or other by-products that are not included in the final weight. Handling mistakes or airflow in the drying apparatus could cause some material to be lost during the drying process, or it could blow away small particles.

The total flotation process and measurements shown in Table 1 are reasonably precise, showing meticulous handling, as described by Ostadrahimi et al., (2021) flotation and Aydin and Kurnaz (2023) product measuring concept.

Table 1: Froth Flotation of Sphalerite/Galena Sample

Material	Selective Reagent	2 g of CS			4 g of CS			6 g of CS		
		Concentrate (g)	Tailings (g)	Total (g)	Concentrate (g)	Tailings (g)	Total (g)	Concentrate (g)	Tailings (g)	Total (g)
ZnS/PbS	CS	189	110	299	219	81	300	235	65	300

3.4 Characterization of Floated Sphalerite/Galena

The concentrates and tailings resulting from the froth flotation of sphalerite/galena were characterized to assess the effectiveness of the CS. As the silicon drift detector (SDD) in the XRF measured the energy and intensity of these fluorescent X-rays, the energy of the X-rays identified the elements contained in the sample, while the intensity of the X-rays measured the concentration of each element. After processing the data, the software of the XRF system produced a spectrum showing the energies and intensities of the detected X-rays which were found to correlate to several elements. The percentage values corresponding to the various elements were then recorded. Table 2 presents the flotation performance of the CS with various concentrations.

Table 2: Characterised Floated Sphalerite/Galena

S/N	Material	2 g of CS		4 g of CS		6 g of CS	
		Concentrate (ppm)	Tailings (ppm)	Concentrate (ppm)	Tailings (ppm)	Concentrate (ppm)	Tailings (ppm)
1	Lead (Pb)	304,597	227,234	408,923	103,323	499,997	1,243
2	Arsenic (As)	18,298	13,370	22,288	7,784	28,285	2,652
3	Zinc (Zn)	139,193	158,426	76,433	215,985	1,125	294,933
4	Copper (Cu)	1,904	1,404	1,781	1,343	1,898	1,399
5	Cobalt (Co)	238	-	238	-	238	-
6	Iron (Fe)	11,995	15,232	12,875	13,992	11,222	15,898
7	Manganese (Mn)	1,323	1,418	1,238	1,499	986	1,755
8	Scandium (Sc)	34	33	33	33	33	33
9	Calcium (Ca)	3,194	4,176	3,057	4,250	2,782	4,542
10	Potassium (K)	371	298	373	290	374	277
11	Antimony (Sb)	5,794	-	5,794	-	5,794	-
12	Sternum (Sn)	1,480	-	1,480	-	1,480	-
13	Cadmium (Cd)	805	-	805	-	805	-
14	Silver (Ag)	1,919	-	1,919	-	1,919	-
15	Chromium (Cr)	91	76	88	77	72	94
16	Titanium (Ti)	-	-	-	-	-	-

Pb was found to be activated with 2 g of CS, as shown by the 304,597 ppm in the concentrate. A higher quantity of Pb, 408,923 ppm, migrated to the concentrate when the CS dosage was increased to 4 g. The Pb concentration increased considerably further to 499,997 ppm when the CS volume was increased to 6 g. It is observed that in the flotation of ZnS/PbS, CS functions as an activator for Pb. This is demonstrated by the Pb concentration in the flotation concentrate increasing as CS is added from 2 g to 4 g and 6 g. This relationship offers useful data for optimizing the use of CS to increase Pb recovery from ore, resulting in more sustainable and effective mineral processing processes.

On the other hand, with 2 g of CS, 158,426 ppm of Zn moved to the tailings. When the dosage was increased to 4 g and 6 g, the concentrations of Zn in the tailings rose to 215,985 ppm and 294,933 ppm, in that order,

leaving less Zn in the concentrates. This statement demonstrates that adding more CS to the flotation process generates a greater quantity of zinc in the tailings rather than in the concentrate, or that increasing the amount of CS in the flotation process produces a higher concentration of zinc in the tailings. This study shows that CS depresses Zn effectively, preventing it from adhering to the froth while separating from Pb as the dosage of CS is increased.

The increase in Pb in the concentrates and Zn concentrations in the tailings with higher CS doses indicate that the flotation process became more efficient at separating Pb from Zn. This demonstrates a trade-off effect on the overall recovery. As higher CS amounts are more effective at sinking Zn, this is required in processing situations where Pb is the target mineral or when selective recovery of Pb over Zn is needed. In addition, if both Pb and Zn are required, the CS quantity must be carefully controlled to optimize the overall economic gain.

The inability for the complete activation or depression by CS in this study could be due to the following reasons: the competing reactions of impurities such as arsenic, copper, iron, manganese, scandium, calcium, and potassium present in the ore might have reduced the availability or activity of the CS towards Pb activation or Zn depression as suggested by Alenezi et al., (2022), hindering the complete adsorption or effectiveness of CS. As opined by Alenezi and Al-Qabandi, (2023), flotation conditions such as pH, temperature, agitation rate, and flotation time usually contribute to the inefficiencies of reagents. The inherent properties of PbS/ZnS, such as surface charge, crystal structure (Huang et al., 2019), and mineral associations as reported by Rasib et al., (2023) can also render materials less responsive to reagents.

Understanding the environmentally friendly, locally sourced organic reagent and its effects as an activator of Pb and a depressant on Zn, CS can help reduce environmental pollution caused by NaCN and Na₂S while also optimizing reagent consumption to ensure economic viability.

4. Conclusion

This study investigated the effectiveness of corn starch in the selective flotation of ZnS/PbS to obtain Zn and Pb. The sieve analysis presented the Zurak-Wase sphalerite/galena particle size in the $-0.71+0.50$ mm range, producing a cumulative 50 percent for ideal liberation. The material using 2 g, 4 g, and 6 g of CS floated 189 g, 219 g and 235 g of concentrates out of 300 g in each case, showing an increase in CS volume increases concentrate in the froth. The XRF characterization demonstrated that with 2 g, 4 g, and 6 g of CS, 304,597 ppm, 408,923 ppm and 499,997 ppm of Pb were activated, and depressed 158,426 ppm, 215,985 pm and 294,933 ppm of Zn. The XRF results show that with an increased amount of CS, more Pb is activated, and more Zn is depressed. Floating with 2 g or 4 g of CS, selective separation could not be effectively achieved potentially due to the competing responses of gangue, and flotation conditions such as pH, temperature, conditioning rate, and agitation time. This study indicates that CS is a good activator of Pb and a depressant of Zn by efficiently separating Pb from Zn, achieving the selective flotation of sulphide minerals using a locally sourced reagent to replace NaCN and Na₂S to mitigate water and environmental pollution. Corn starch shows the capability for activating gangue such as Co, Sb, Sn, Cd, Ag and Ti. Even at higher amounts, CS could not depress any of these substances, making it their excellent activator. It is recommended that mineral and chemical engineering processes can test the outcomes of this study for the selective flotation of Pb from Zn. The amount of CS be increased even beyond the 6 g to effectively promote hydrophobicity on Pb and hydrophilicity on Zn. To improve separability, subsequent studies could investigate raising agitation time, temperature, and pH, changing the surface charge to guarantee chemical interactions and using Atomic Absorption Spectrophotometry (AAS) for characterization.

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