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Investigation of lead depression in an antimony flotation circuit

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Abstract: Antimony is a strategic metal defined as a critical raw material by the European Union. One key factor determining the quality of antimony concentrates is impurity levels, with lead (Pb) content playing a particularly restrictive role in both marketability and metallurgical performance. The literature has tested various reagents, such as sodium metabisulfite, polysaccharides, and dichromates, for Pb depression across different ore types and reported their effects on selectivity. At the Eti Bakır Halıköy Plant, periodic increases in Pb grade have been observed, degrading concentrate quality and prompting laboratory- and plant-scale flotation experiments to address this issue. The results demonstrated that among the reagents tested, sodium metabisulfite was the most effective compound for Pb depression. Under laboratory conditions, the Pb content of the antimony concentrate was significantly reduced with the use of sodium metabisulfite. Plant-scale trials similarly showed that the Pb content of the concentrate decreased by nearly half. These findings indicate that sodium metabisulfite is an effective reagent for Pb depression in antimony flotation circuits and that its plant-scale application can improve concentrate quality.

Keywords: antimony, lead depression, flotation, depressants, concentrate quality

1. Introduction

Antimony (Sb) is a critical metalloid used in various strategic applications, including flame retardants, alloys, electronic components, and energy storage systems (USGS, 2024). The European Union has designated antimony as a critical raw material because of its limited global availability and the concentration of production in certain geographic regions (European Commission, 2020). This situation makes the efficient utilization of antimony ores and the production of high-quality concentrates strategically important. Froth flotation is widely used to beneficiate sulfide antimony ores. However, antimony flotation involves significant selectivity problems because sulfide impurity minerals associated with stibnite (Sb_2S_3) exhibit similar surface properties (Özer, 2022). In particular, the flotation of Pb-bearing minerals (e.g., galena and Pb-bearing sulfosalts) together with stibnite can increase Pb contamination in antimony concentrates (Segura-Salazar and Brito-Parada, 2021).

High Pb impurities in antimony concentrates increase slag formation (i.e., slagging/refining load) during pyrometallurgical processing and may lead to additional Sb losses to slag (Anderson, 2012; Moosavi-Khoonsari et al., 2022). Therefore, Pb depression has emerged as a fundamental process challenge, especially since some smelters impose strict Pb limits for stibnite concentrates (Segura-Salazar and Brito-Parada, 2021). The literature reports various approaches to Pb depression, including strong oxidizing depressants such as dichromates, polysaccharide-based reagents, sulfidizing and reducing reagents, and optimization strategies based on pH and particle size (Bulatovic, 2007; Nyakubaya et al., 2016).

In this study, the effects of pH, particle size, and different reagent types -specifically comparing potassium dichromate, starch, and sodium metabisulfite (SMBS)- on the control of Pb impurities limiting concentrate quality in the antimony flotation circuit of the Eti Bakır Halıköy Plant were investigated through laboratory-scale flotation experiments. The reagent that showed the most promising performance in depressing Pb-bearing phases was subsequently applied at an industrial scale under plant operating conditions to confirm the laboratory-scale findings. These findings provide

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useful guidance for process optimization strategies to reduce Pb impurities in antimony flotation circuits.

2. Materials and methods

2.1. Materials

This study was carried out on an antimony ore sample obtained from the Eti Bakır Halıköy Plant located in the Beydağ district of İzmir, Türkiye. The flotation feed sample used in the experiments was selected to represent operating periods during which Pb impurities adversely affected concentrate quality at the plant. The As, Sb, Pb, and Fe contents of the flotation feed sample were determined using ICP-OES after appropriate sample digestion, whereas the S content was measured by combustion at 950 °C. Table 1 presents the analytical results.

Table 1. Chemical analysis of the flotation feed

Element	Sb	Pb	As	S	Fe
Content, mass (%)	4.17	0.18	0.25	4.40	2.72

Mineralogical characterization studies were carried out using scanning electron microscopy equipped with a Mineral Liberation Analyzer (SEM–MLA) system to determine the distribution of antimony and gangue minerals in the flotation feed. Modal mineralogical analyses were conducted on the −212+150 µm, −150+106 µm, −106+75 µm, −75+53 µm, −53+38 µm, and −38+20 µm size fractions, which represent the particle size range relevant to flotation. Table 2 presents the results of the modal mineralogical analyses. Quartz is the dominant mineral in all investigated size fractions, generally occurring at proportions exceeding 70%. Antimony occurs in the ore almost entirely as stibnite, varying from about 5% to 14% across all size fractions. Sulfide minerals, mainly pyrite, accompanied by minor amounts of arsenopyrite, occur as associated phases and are generally present at levels below 10%. Lead-bearing minerals occur at minor proportions and are mainly represented by oxidized and secondary Pb phases, predominantly wulfenite, with subordinate amounts of anglesite and clausthalite–galena. Oxide minerals represented by jacobsite–magnetite are observed at low proportions in all size fractions, whereas carbonate minerals such as dolomite–ankerite, along with clay and silicate gangue minerals including muscovite, illite, and smectite, are found at relatively higher proportions, particularly in the finer size fractions.

Table 2. Modal mineralogical analysis results of the sample

Modal Mineralogy						
Mineral, Mass (%)	-212+150 (µm)	-150+106 (µm)	-106+75 (µm)	-75+53 (µm)	-53+38 (µm)	-38+20 (µm)
Stibnite	13.91	8.70	8.15	6.09	5.10	6.40
Quartz	67.74	76.28	75.29	75.20	76.23	69.51
Pyrite	8.27	6.18	6.14	5.32	5.38	7.05
Muscovite	1.96	2.43	3.96	6.72	6.18	9.07
Jacobsite-Magnetite	1.90	1.51	1.17	1.43	1.64	2.10
Arsenopyrite	0.30	0.15	0.04	0.15	0.13	0.21
Dolomite-Ankerite	0.43	0.62	0.63	0.65	0.94	1.04
Illite	0.71	0.64	0.63	0.56	0.52	0.40
Smectite	0.94	0.87	0.92	0.91	0.95	0.86
Wulfenite	0.37	0.09	0.18	0.07	0.09	0.08
Anglesite	0.10	0.09	0.07	0.05	0.05	0.05
Clausthalite-Galena	0.11	0.03	0.06	0.03	0.04	0.08
Others	3.26	2.41	2.76	2.82	2.74	3.15
Total	100.00	100.00	100.00	100.00	100.00	100.00

Table 3 presents the distribution of Pb-bearing mineral phases in the flotation feed. The Pb-bearing phases were dominated by wulfenite, which accounted for 60.61% of the total Pb-bearing phases. Anglesite was the second most abundant Pb-bearing phase, accounting for 19.59%, followed by an unidentified Pb-bearing phase at 10.43%. Since this MLA-based phase assignment could not be independently verified by additional chemical or mineralogical analysis, it was reported as an unidentified Pb-bearing phase in the present study. Pb also occurred in lower proportions as clausthalite–galena and elemental Pb, accounting for 7.04% and 2.33%, respectively. The predominance of wulfenite and anglesite indicates that Pb in the ore is mainly associated with oxidized and secondary Pb-bearing phases, which is an important factor influencing Pb flotation behavior and the selection of appropriate depression strategies.

Table 3. Distribution of Pb-bearing mineral phases identified in the flotation feed based on mineralogical analysis

Pb-Bearing Minerals (%)				
Wulfenite	**Anglesite**	**Clausthalite-Galena**	**Lead**	**Unidentified Pb-bearing phase**
60.61	19.59	7.04	2.33	10.43

In this study, different types of reagents were used to depress the lead (Pb) content in the concentrate obtained from the antimony flotation circuit. The reagents utilized in this study were divided into collectors, activators, and depressants, with a primary focus on the impact of depressants on flotation behavior. In plant operations, Aero 3477 is used as the collector, a sodium dialkyl dithiophosphate-based reagent (Cytec, 2010). Lead nitrate is utilized as an activator in the plant to promote the activation of antimony-bearing mineral phases. Aero 3477 was supplied by Syensqo. Lead(II) nitrate ($Pb(NO_3)_2$, 99% purity, ZAG Kimya) and copper sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$, Emboy) were used as activators. Potassium dichromate ($K_2Cr_2O_7$, Merck), sodium metabisulfite ($Na_2S_2O_5$, ≥99.5% purity, Merck), and soluble starch supplied by Carlo Erba Reagents were used as depressant reagents.

In this study, copper sulfate was evaluated as an alternative activator to lead nitrate. Copper sulfate ($CuSO_4$) is widely used as an activator in sulfide flotation circuits because it modifies mineral surface chemistry to enhance collector–mineral interactions and improve activation (Bulatovic, 2007). Potassium dichromate ($K_2Cr_2O_7$) is an oxidizing agent that modifies the surface properties of lead-bearing minerals, reducing their floatability, especially in systems containing galena (Bulatovic, 2007; Zeng et al., 2025). Starch and other polysaccharide-based depressants have been extensively studied as selective depressants in flotation systems. They can adsorb onto mineral surfaces, increase surface hydrophilicity, and consequently reduce the floatability of both sulfide and oxide mineral phases. In Pb-bearing systems, polysaccharide-based depressants have been investigated to reduce Pb recovery and Pb grade in the concentrate, thereby improving flotation selectivity (Bulatovic, 2007; Qin et al., 2013; López-Valdivieso et al., 2017). Sodium metabisulfite ($Na_2S_2O_5$) is a commonly used depressant in sulfide mineral flotation systems because of its reducing character (Semoto et al., 2021).

2.2. Methods

Flotation experiments were conducted using a Denver-type laboratory flotation machine to replicate the rougher and cleaner flotation stages employed in plant operations. Open-circuit flotation tests were performed throughout the experimental program. The flotation tests were carried out in three sequential stages, each utilizing different cell volumes, impeller speeds, and air flow rates. Rougher flotation was performed in a 2.2 dm^3 cell at an impeller speed of 1100 rpm with an air flow rate of 2.0 dm^3/min. The first cleaner stage was conducted in a 1.2 dm^3 cell at 850 rpm with an airflow rate of 1.5 dm^3/min, whereas the second cleaner stage was carried out in a 0.9 dm^3 cell at 700 rpm with an airflow rate of 1.0 dm^3/min. Rougher flotation tests were performed at a pulp concentration of 30–35% solids by weight, while cleaner flotation tests were carried out at approximately 20% solids by weight.

The reference flotation tests were conducted under plant operating conditions, using Aero 3477 as the collector at 110 g/Mg and lead nitrate as the activator at 90 g/Mg. A conditioning time of 5 min was applied to reflect the plant operating conditions. These reference tests were carried out at the plant grinding size (d_{80} = 130 µm) and within the plant operating pH range of 6.0–6.5.

In addition to the reference flotation tests, separate pH and particle size tests were performed to evaluate their effects on flotation performance. Initially, pH tests were conducted under plant-based reference reagent conditions at pH values of 6, 7, 8, and 9. Subsequently, particle size tests were carried out by grinding the ore sample to the plant grinding size, d_{80} = 130 µm, and to a finer size, d_{80} = 75 µm, to assess whether increased grinding would enhance stibnite liberation and alter the flotation behavior of Pb-bearing mineral phases.

Based on the pH and particle-size test outcomes, further reagent evaluation experiments were carried out at d_{80} = 130 µm and pH 6.0–6.5 to investigate Pb depression behavior. In these tests, copper sulfate was evaluated as an alternative activator, while starch, potassium dichromate, and sodium metabisulfite were evaluated as depressant reagents at different dosage levels. Copper sulfate, starch, and potassium dichromate were prepared as 10% aqueous solutions. Starch and potassium dichromate were added before the activator and collector, followed by 10 min of conditioning. In the pH, particle size, and activator evaluation tests, the activator and Aero 3477 collector were added and conditioned for 5 min, in accordance with plant operating conditions. Sodium metabisulfite was added during the grinding stage. All laboratory flotation tests were conducted using tap water, and no separate frother was added.

Table 4. All the flotation parameters in the experiments

Parameter	Value
Flotation machine	Denver-type
Grind size, d_{80}	75 µm and 130 µm
Rougher pulp concentration	30–35%
Cleaner pulp concentration	20%
pH range	6–9
Conditioning time (min.)	5 and 10
Collector	Aero 3477
Activators	$Pb(NO_3)_2$ and $CuSO_4$
Depressants	Starch, $K_2Cr_2O_7$ and SMBS

In summary, these laboratory flotation tests were conducted to compare the effects of pH, particle size, activator type, and depressant dosage on Sb–Pb flotation selectivity. All tests were performed under controlled and fixed operating conditions to ensure a consistent comparison between the tested conditions. Selected promising conditions were repeated for internal verification before selecting the reagent condition for plant-scale evaluation; however, replicate tests were not performed systematically for all conditions. The reagent condition that gave the most favorable Pb depression performance was then selected for plant-scale evaluation under industrial operating conditions.

3. Results and discussion

3.1. Flotation tests at different pH values

Pulp pH is a key control variable in antimony flotation because it affects mineral surface properties and reagent adsorption, thereby influencing the floatability of Sb- and Pb-bearing mineral phases and overall flotation selectivity. To determine the suitable pH range for the flotation experiments, single-stage rougher flotation tests were conducted at pH 6, 7, 8, and 9. The pulp pH was adjusted using lime (CaO). The flotation products were evaluated based on Sb and Pb grades and recoveries. The tests were conducted using plant-based reference reagent conditions. Aero 3477 was used as the collector at 110 g/Mg, and lead nitrate as the activator at 90 g/Mg. The conditioning time for the tests was 5 min. Other flotation parameters, including particle size (d_{80} = 130 μm), pulp concentration (30–35% solids by weight), and flotation time, were kept constant throughout the pH experiments.

Table 5. Effect of pH on Sb and Pb grades and recoveries

pH	Grade (%)		Recovery (%)	
	Sb	Pb	Sb	Pb
6	37.49	0.09	92.04	36.84
7	22.28	0.09	50.68	38.33
8	19.00	0.11	35.15	29.48
9	18.74	0.17	34.01	34.40

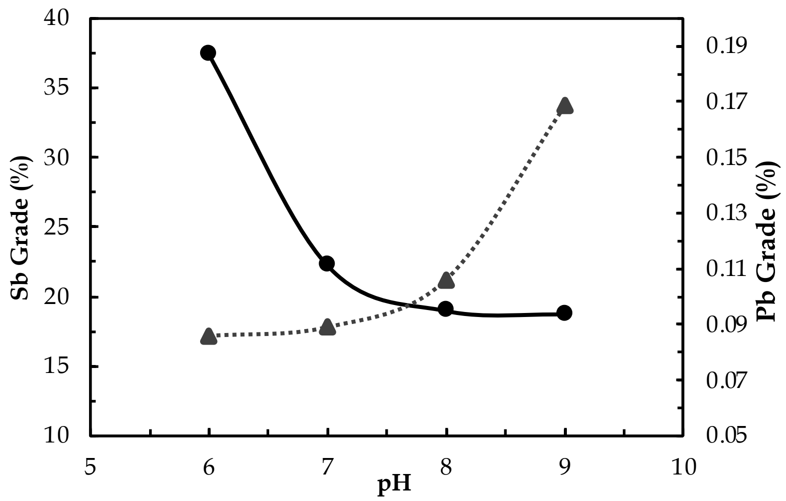

Fig. 1. Variation of Sb and Pb grades in the flotation concentrate as a function of pulp pH under fixed flotation conditions (d_{80} = 130 μm, Aero 3477 dosage = 110 g/Mg, and $Pb(NO_3)_2$ dosage = 90 g/Mg).

The pH-dependent flotation response was evaluated using both concentrate grades and recoveries. The most favorable flotation response was obtained at pH 6, where the Sb grade and Sb recovery reached 37.49% and 92.04%, respectively (Table 5 and Fig. 1). Increasing the pH from 6 to 7 decreased the Sb grade from 37.49% to 22.28% and the Sb recovery from 92.04% to 50.68%. This sharp decrease within a single pH unit indicates that stibnite flotation in this ore is highly sensitive to the pH range of 6–7.

This behavior may reflect the pH-dependent surface properties of stibnite. The contact angle of stibnite has been reported to remain relatively stable under acidic conditions and to decrease as the pulp becomes alkaline, which is associated with the formation of SbOH and SH sites in equilibrium with SbO^- and S^- sites, depending on pH (Segura-Salazar and Brito-Parada, 2021). This change indicates increased ionic and hydrophilic character of the stibnite surface, which may reduce collector-induced hydrophobicity. In addition, dialkyl dithiophosphate collectors have been reported to perform more effectively under acidic pH conditions in stibnite flotation (Segura-Salazar and Brito-Parada, 2021). Since powdered lime (CaO) was used for pH adjustment, a possible contribution of Ca-bearing species to the observed pH-dependent response cannot be completely excluded; however, the pronounced decrease in Sb grade and recovery is primarily interpreted in relation to the pH-dependent surface properties and hydrophobicity of stibnite. Therefore, the pH range of 6.0–6.5, which corresponds to the plant operating conditions, was selected for the subsequent particle size and reagent evaluation tests.

3.2. Flotation tests at different particle sizes

Particle size is an important flotation parameter because it affects mineral liberation, particle–bubble interactions, and the recovery of valuable and impurity-bearing mineral phases. In antimony flotation, inadequate liberation at coarse sizes can limit stibnite recovery. In contrast, the excessive generation of fine particles may increase the recovery of impurity-bearing phases and negatively affect flotation selectivity. The SEM–MLA results indicated that stibnite was less abundant in the finer size fractions, while Pb-bearing minerals, particularly wulfenite, were relatively more concentrated in the coarser fractions. Therefore, two particle size conditions were compared in this study: the plant operating particle size, d_{80} = 130 µm, which was used as the reference condition, and a finer particle size, d_{80} = 75 µm, which was tested to evaluate whether decreasing the particle size would reduce the Pb grade and Pb recovery in the concentrate. Since only two particle size conditions were tested, the results should be interpreted as a comparison between the plant operating particle size and a finer particle size condition, rather than as a complete particle-size optimization trend. Table 5 presents the results.

Table 6. Effect of particle size on Sb and Pb grades and recoveries

Particle Size (µm)	Grade (%)		Recovery (%)	
	Sb	Pb	Sb	Pb
130	61.31	2.20	27.18	25.58
75	59.78	2.17	55.45	51.70

Decreasing the particle size from d_{80} = 130 µm to d_{80} = 75 µm increased Sb recovery from 27.18% to 55.45% (Table 6). However, Pb recovery also increased from 25.58% to 51.70%. In contrast, the concentrate grades changed only slightly; Sb grade decreased from 61.31% to 59.78%, while Pb grade remained almost unchanged, decreasing only from 2.20% to 2.17%. This response indicates that finer particle size increased recovery of both Sb- and Pb-bearing phases but did not clearly improve Sb–Pb selectivity.

From a flotation-mechanism perspective, this response should not be interpreted solely as improved true flotation due to better liberation. Fine-particle recovery in flotation may result from both true flotation and mechanical entrainment, and entrainment is closely related to the mechanical carryover of particles with water into the froth product (Konopacka and Drzymala, 2010; Wang et al., 2015). Therefore, the simultaneous increase in Sb and Pb recoveries at d_{80} = 75 µm may reflect a combined effect of improved recovery of stibnite-bearing particles, recovery of composite or associated Pb-bearing particles, and possible entrainment of fine particles.

Because water recovery, froth stability, and size-by-size mineralogical analysis of the flotation products were not measured, the individual contributions of true flotation and entrainment could not be quantified. Nevertheless, the nearly unchanged concentrate grades, together with the simultaneous increase in both Sb and Pb recoveries, indicate that reducing the particle size to d_{80} = 75 µm did not provide a clear advantage in reducing Pb recovery to the concentrate. Therefore, the plant grinding size of d_{80} = 130 µm was considered more suitable for the subsequent Pb depression tests, where minimizing Pb recovery was the primary objective.

3.3. Reagent effect for Pb depression

3.3.1. Effect of copper sulfate

In the plant-based reference flotation scheme, Aero 3477 was used as the collector at 110 g/Mg, and lead nitrate as the activator at 90 g/Mg. Under these conditions, Pb-bearing mineral phases were also recovered in the concentrate to some extent, indicating limited Sb–Pb selectivity. Because lead nitrate may activate both stibnite and associated Pb-bearing phases, copper sulfate was evaluated as an alternative activator. The $CuSO_4$ dosage of 500 g/Mg was selected with reference to a previous flotation study on a complex antimony ore, where the same $CuSO_4$ dosage was used. (Gülcan et al., 2019). The $CuSO_4$ test was conducted at d_{80} = 130 µm and pH 6.0–6.5, with 10 min of conditioning before flotation, under otherwise identical flotation conditions.

The comparison between $Pb(NO_3)_2$ and $CuSO_4$ was not performed on an equimolar basis, and no dose–response curve was generated for the two activators. Therefore, the results should be interpreted as a comparison between the plant-based $Pb(NO_3)_2$ reference condition and a selected $CuSO_4$ test condition, rather than as a complete activator optimization study. Table 6 and Figure 2 present the results.

Table 7. Effect of activator type on Sb and Pb grades and recoveries in antimony flotation

Activator	**Grade (%)**		**Recovery (%)**	
	Sb	**Pb**	**Sb**	**Pb**
$Pb(NO_3)_2$	61.31	2.20	27.18	25.58
$CuSO_4$	59.17	2.00	39.58	33.25

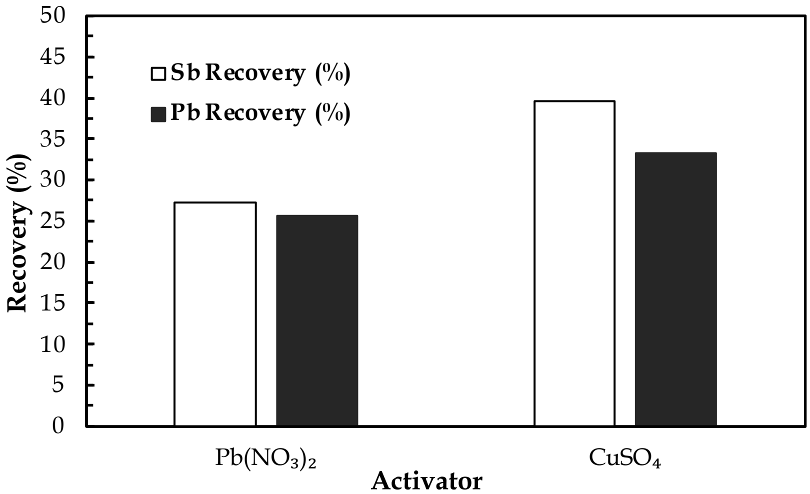

Fig. 2. Effect of activator type on Sb and Pb recoveries in antimony flotation.

Under the selected $CuSO_4$ condition, Sb recovery increased from 27.18% to 39.58% compared with the base lead nitrate reference condition (Table 7 and Fig. 2). This increase indicates that $CuSO_4$ enhanced the flotation response of antimony-bearing phases under the tested conditions. However, Pb recovery also increased from 25.58% to 33.25%, showing that the improvement in Sb recovery was accompanied by increased recovery of Pb-bearing phases. Although the concentrate Pb grade decreased slightly from 2.20% to 2.00%, the simultaneous increase in Pb recovery indicates that $CuSO_4$ alone did not provide sufficient Sb–Pb selectivity. Therefore, the selected $CuSO_4$ condition was not further optimized, and subsequent tests focused on depressant reagents to improve Pb control and Sb–Pb separation selectivity.

3.3.2. Effect of potassium dichromate

To evaluate the effect of potassium dichromate on Pb depression, flotation tests were conducted by adding potassium dichromate to the plant-based reference reagent scheme, consisting of Aero 3477 as the collector at 110 g/Mg and lead nitrate as the activator at 90 g/Mg. Potassium dichromate was evaluated at dosages of 500, 1000, and 2000 g/Mg, with a conditioning time of 10 minutes before flotation. The tests were conducted at d_{80} = 130 µm and pH 6.0–6.5. The flotation performance was evaluated in terms of Sb and Pb grades and recoveries. Table 8 and Fig. 3 present the results.

Adding potassium dichromate caused a pronounced decrease in Pb recovery, indicating that dichromate effectively depressed the floatability of Pb-bearing mineral phases. However, potassium dichromate also adversely affected Sb recovery, and at higher dosages, the system showed a non-selective over-depression response. Among the tested dosages, 1000 g/Mg $K_2Cr_2O_7$ produced the lowest Pb grade, decreasing it from 2.20% under the baseline flotation condition to 1.03%. At the same dosage, Pb recovery decreased from 25.58% to 5.97%, while Sb recovery also decreased from 27.18% to 10.20%, and Sb grade decreased to 31.56%. These results indicate that although potassium dichromate can reduce Pb recovery and Pb grade, its non-selective depression of stibnite limits its applicability for improving Sb–Pb separation selectivity.

Table 8. Effect of potassium dichromate dosage on Sb and Pb grades and recoveries in antimony flotation

Potassium dichromate dosage (g/Mg)	Grade (%)		Recovery (%)	
	Sb	Pb	Sb	Pb
0 (Base)	61.31	2.20	27.18	25.58
500	36.94	1.20	5.57	4.09
1000	31.56	1.03	10.20	5.97
2000	31.37	1.24	4.29	4.02

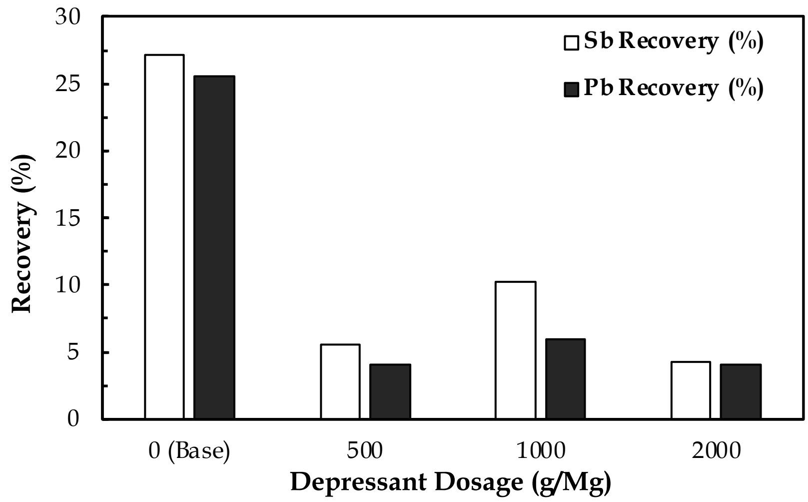

Fig. 3. Effect of potassium dichromate dosage on Sb and Pb recoveries in antimony flotation

3.3.3. Effect of starch

Starch is a polysaccharide-based depressant widely used in flotation systems to depress the floatability of selected mineral phases. In this study, the effect of starch on the control of Pb-bearing phases in antimony flotation was investigated by adding starch at different dosages to the base flotation condition. Starch was tested at dosages of 500, 1000, and 1500 g/Mg, and the pulp was conditioned for 10 min before flotation. The tests were conducted at d_{80} = 130 µm and pH 6.0–6.5. The flotation performance was evaluated in terms of Sb and Pb grades and recoveries. Table 8 and Fig. 4 present the results.

Starch dosage affected Sb–Pb flotation selectivity differently depending on the applied dosage, as evaluated using concentrate grade and recovery data (Table 9 and Fig. 4). At 500 g/Mg starch, both Sb

Table 9. Effect of starch dosage on Sb and Pb grades and recoveries in antimony flotation

Starch dosage (g/Mg)	Grade (%)		Recovery (%)	
	Sb	Pb	Sb	Pb
0 (Base)	61.31	2.20	27.18	25.58
500	55.26	2.61	64.43	67.06
1000	59.55	1.92	23.02	17.52
1500	57.09	2.43	54.60	53.89

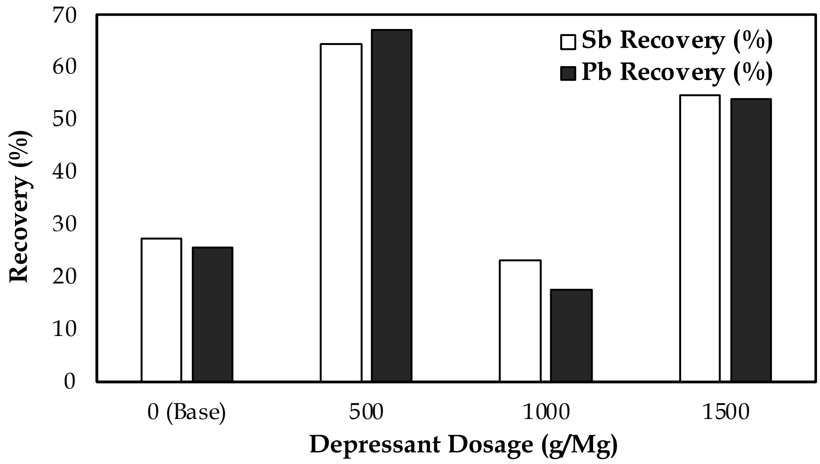

Fig. 4. Effect of starch dosage on Sb and Pb recoveries in antimony flotation

and Pb recoveries increased compared with the baseline flotation condition, while the Pb grade of the concentrate also increased. This result indicates that starch was not selective for Pb depression at this dosage, since the increase in Sb recovery was accompanied by higher Pb recovery and Pb grade.

Increasing the starch dosage to 1000 g/Mg reduced Pb recovery from 25.58% to 17.52% and decreased the Pb grade from 2.20% to 1.92%, indicating improved Pb depression. However, this improvement was accompanied by a decrease in Sb recovery to 23.02%, suggesting that the depressing action of starch was not fully selective toward Pb-bearing phases. At 1500 g/Mg, both Sb and Pb recoveries increased again, indicating poorer Sb–Pb selectivity and greater reporting of Pb-bearing phases to the antimony concentrate. Overall, starch showed limited Pb depression at 1000 g/Mg; however, the decrease in Sb recovery indicates that starch alone did not provide sufficient selectivity for effective Sb–Pb separation under the tested conditions.

3.3.4. Effect of sodium metabisulfite

Sodium metabisulfite (SMBS) is a reducing reagent widely used in sulfide flotation systems to control mineral surface oxidation and depress selected impurity-bearing mineral phases. In this study, the effect of SMBS on the depression of Pb-bearing phases in antimony flotation was evaluated by adding SMBS to the base flotation conditions at dosages of 1500 and 2000 g/Mg. The tests were conducted at d_{80} = 130 µm and pH 6.0–6.5. Table 9 and Fig. 5 present the results.

Sodium metabisulfite markedly improved Sb–Pb flotation selectivity at the selected dosage of 1500 g/Mg, as evaluated using concentrate grade and recovery data (Table 9 and Fig. 5). The addition of sodium metabisulfite substantially reduced Pb recovery compared with the baseline flotation condition, indicating effective depression of Pb-bearing phases reporting to the concentrate. At 1500 g/Mg SMBS, Pb recovery decreased from 25.58% to 4.42%, while the Pb grade of the concentrate decreased from 2.20% to 0.58%. Under the same conditions, the Sb grade was largely maintained, decreasing only from 61.31% to 60.29%; however, Sb recovery decreased from 27.18% to 20.63%. Increasing the sodium metabisulfite dosage to 2000 g/Mg did not further improve Pb depression, as both Pb grade and Pb recovery increased relative to the 1500 g/Mg test.

Table 10. Effect of sodium metabisulfite dosage on Sb and Pb grades and recoveries in antimony flotation

Sodium metabisulfite dosage (g/Mg)	Grade (%)		Recovery (%)	
	Sb	Pb	Sb	Pb
0 (Base)	61.31	2.20	27.18	25.58
1500	60.29	0.58	20.63	4.42
2000	65.46	1.35	20.55	7.74

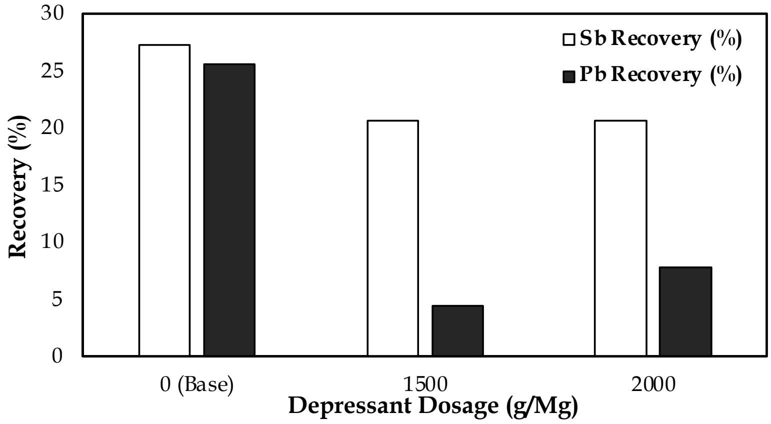

Fig. 5. Effect of sodium metabisulfite dosage on Sb and Pb recoveries in antimony flotation

The improved depression of Pb-bearing phases obtained with SMBS may be associated with its role as a reducing and conditioning reagent that modifies pulp chemistry and mineral–solution interfacial conditions. In flotation systems, reagent adsorption at the solid–liquid interface governs the hydrophobic or hydrophilic character of mineral surfaces and therefore controls flotation selectivity (Leja, 1981; Bulatovic, 2007). Metabisulfite treatment has been reported to produce sulfate species mainly through reaction with dissolved oxygen in water, and the formation of hydrophilic surface products has been associated with reduced mineral floatability (Semoto et al., 2021). In the present study, this mechanism is important because the Pb-bearing phases in the flotation feed were dominated by oxidized and secondary Pb minerals, mainly wulfenite and anglesite, whereas galena-bearing phases occurred only in minor amounts. Since SMBS was added during the grinding stage, it may have modified the chemical environment before flotation and promoted more hydrophilic surface conditions on Pb-bearing phases. Under the subsequent dithiophosphate-based flotation conditions, this surface modification may have weakened the interaction between Pb-bearing surfaces and the collector, thereby reducing the floatability of Pb-bearing phases. However, since direct surface analyses were not performed in this study, the proposed mechanism should be considered an interpretation based on flotation response and mineralogical evidence rather than a confirmed surface reaction pathway.

These results indicate that sodium metabisulfite provided the most favorable Sb–Pb selectivity among the tested depressant dosages at 1500 g/Mg. Although Sb recovery declined slightly, the substantial decrease in Pb grade and Pb recovery shows that sodium metabisulfite was the most effective depressant for controlling Pb-bearing impurities in the antimony flotation circuit under the tested conditions.

3.3.5. Comparative evaluation of selected reagent conditions

To allow direct comparison of the tested reagent conditions, Table 11 summarizes representative conditions from the reagent test series presented in the preceding sections. The comparison focused on Sb grade, Pb grade, Sb recovery, Pb recovery, and the Sb/Pb recovery selectivity ratio. The selected dosages represent the most relevant conditions for evaluating Pb depression performance and Sb–Pb flotation selectivity under the tested conditions.

SMBS at 1500 g/Mg provided the most favorable Sb–Pb flotation selectivity among the selected reagent conditions (Table 11). The Sb/Pb recovery selectivity ratio obtained with SMBS was 4.67, which was higher than those obtained with $K_2Cr_2O_7$, starch, and $CuSO_4$, with values of 1.71, 1.31, and 1.19, respectively. In addition, SMBS produced the lowest Pb grade and Pb recovery, reducing them to 0.58% and 4.42%, respectively. Under the same conditions, Sb grade remained at 60.29%, close to the baseline value of 61.31%.

In contrast, $CuSO_4$ increased Sb recovery; however, this improvement was accompanied by increased Pb recovery, indicating that the selectivity gain was limited under the selected $CuSO_4$ condition. Potassium dichromate reduced both Pb grade and Pb recovery; however, it also substantially decreased Sb grade and Sb recovery. At 1000 g/Mg $K_2Cr_2O_7$, the Sb grade decreased to 31.56%, indicating a substantial loss in concentrate quality and a non-selective depression effect. This response limits the suitability of $K_2Cr_2O_7$ for industrial application under the tested conditions. Starch showed a moderate Pb depression response at 1000 g/Mg, but its Sb/Pb recovery selectivity ratio remained considerably lower than that obtained with SMBS. Overall, the comparative results confirm that SMBS at 1500 g/Mg was the most effective reagent condition for reducing the reporting of Pb-bearing phases to the antimony concentrate under the tested conditions.

Table 11. Comparative performance of selected reagent conditions in Pb depression tests

Reagent	Selected Dosage (g/Mg)	Sb Grade (%)	Pb Grade (%)	Sb Recovery (%)	Pb Recovery (%)	Sb/Pb Selectivity Ratio
Baseline, ($Pb(NO_3)_2$)	90	61.31	2.20	27.18	25.58	1.06
$CuSO_4$	500	59.17	2.00	39.58	33.25	1.19
$K_2Cr_2O_7$	1000	31.56	1.03	10.20	5.97	1.71
Starch	1000	59.55	1.92	23.02	17.52	1.31
SMBS	1500	60.29	0.58	20.63	4.42	4.67

3.4. Plant trial results

Sodium metabisulfite (SMBS), which provided the best Pb-depression performance in laboratory-scale flotation tests, was subsequently applied at an industrial scale under normal plant operating conditions. In the plant trial, SMBS was added to the grinding circuit at 1500 g/Mg to precondition before flotation, and the application was maintained for one week during a period of elevated Pb grade in the plant feed. Since the available plant assay data were reported as weekly composite averages rather than shift-based values, the plant-scale evaluation was performed using weekly average feed and concentrate grades, together with the corresponding enrichment ratios. This method enabled the assessment of SMBS performance in reducing the Pb grade of the antimony concentrate under high-Pb feed conditions.

The laboratory-scale SMBS test results and the plant-scale SMBS trial results are not directly comparable in terms of absolute concentrate grades. The laboratory tests were conducted as open-circuit flotation tests consisting of rougher flotation followed by two cleaner stages, whereas the industrial plant operates as a closed-circuit flotation system including rougher, scavenger, and cleaner stages. In addition, feed grade differences between the laboratory sample and the plant trial feed should also be considered when interpreting the differences between laboratory and plant concentrate grades. Therefore, the observed differences are mainly attributed to feed grade variation, circuit configuration, operating scale, residence time, and circulating streams.

Table 12. Plant-scale comparison of weekly average feed and concentrate grades and enrichment ratios under baseline reference and SMBS application conditions

Condition	Evaluation Period	Feed Grade		Concentrate Grade		Enrichment Ratio (ER)		Recovery
		Pb, %	Sb,%	Pb, %	Sb,%	Pb	Sb	Sb, %
Baseline	Selected high-Pb operating week	0.17	2.89	3.58	68.53	21.06	23.71	~95
SMBS, 1500 g/Mg	One-week SMBS application period	0.27	2.88	1.45	69.01	5.37	23.96	~95

Note: Plant data are reported as weekly composite average values. The baseline reference condition represents a selected high-Pb operating week from the same ore type. Although the feed Pb grade during the SMBS trial was higher than that of the baseline reference condition, this baseline was the closest available non-SMBS reference for comparison under high-Pb feed conditions. Sb recovery values are approximate plant-record values. ER was calculated as the ratio of concentrate grade to feed grade.

The plant-scale results support the effectiveness of SMBS in reducing the Pb grade of the antimony concentrate under industrial operating conditions (Table 12). Under the baseline reference condition without SMBS, the feed Pb grade was 0.17%, while the concentrate Pb grade was 3.58%. During the one-week SMBS application period, the feed Pb grade increased to 0.27%; nevertheless, the concentrate Pb grade decreased to 1.45%. The decrease in concentrate Pb grade from 3.58% to 1.45%, despite the increase in feed Pb grade from 0.17% to 0.27%, indicates that SMBS limited the reporting of Pb-bearing phases to the antimony concentrate under plant-scale operating conditions.

The reduction in the Pb enrichment ratio from 21.06 under the baseline reference condition to 5.37 during SMBS application further confirms improved Pb control. In contrast, the Sb enrichment ratio remained nearly unchanged, changing only from 23.71 to 23.96. Similarly, the Sb grade of the concentrate remained high, increasing slightly from 68.53% to 69.01%. Approximate plant-record values also indicated that Sb recovery remained at about 95% during both periods. These results show that SMBS substantially reduced the Pb grade of the antimony concentrate without adversely affecting Sb concentrate quality, Sb enrichment behavior, or plant-scale Sb recovery.

Overall, the plant trial supported the laboratory-scale findings and showed that SMBS preconditioning in the grinding circuit is a practical strategy for controlling Pb impurities in antimony flotation circuits, particularly during periods of elevated Pb grade in the plant feed.

4. Conclusions

In this study, flotation investigations were conducted at both laboratory and plant scales to reduce lead (Pb), a major impurity that limits concentrate quality in an antimony flotation circuit. The effects of pH, particle size, and reagent type on Pb depression behavior were evaluated using grade and recovery data together with graphical comparisons of Sb and Pb recoveries.

Laboratory-scale experiments demonstrated that pulp pH is a key parameter governing selectivity in antimony flotation, with lower pH conditions providing better concentrate quality and more limited Pb reporting to the concentrate. Particle size tests showed that although finer grinding enhanced Sb recovery, it also increased Pb recovery; therefore, operating at the plant-representative particle size provided more balanced flotation performance. The comparison of activator types showed that copper sulfate was more effective than lead nitrate in enhancing antimony recovery. However, this increase in recovery also increased lead recovery, indicating that copper sulfate alone did not provide sufficient selectivity between antimony and lead. Since the copper sulfate test was not performed on an equimolar basis and no dose–response curve was generated, this result should be interpreted as the response of a selected copper sulfate condition rather than as a complete activator optimization.

Among the reagents evaluated, potassium dichromate effectively depressed Pb; however, its non-selective depression of stibnite significantly reduced Sb grade and recovery. Moreover, the toxicity and environmental concerns associated with dichromate-based depressants limit their applicability in industrial flotation circuits and make them less desirable from a sustainability perspective (Jiao et al., 2022). Despite its ability to reduce lead levels, potassium dichromate was not deemed suitable for industrial use.

The addition of starch partially restricted Pb transfer at certain dosages; however, its adverse effect on Sb recovery and its narrow optimum operating window resulted in limited selectivity. In contrast, sodium metabisulfite (SMBS) effectively suppressed the flotation behavior of Pb-bearing phases while largely preserving Sb recovery. Screening tests, therefore, identified SMBS as the most selective depressant among those tested. In laboratory-scale flotation tests, SMBS reduced the Pb grade of the antimony concentrate from 2.20% to 0.58% and decreased Pb recovery from 25.58% to 4.42%.

Plant-scale application supported the laboratory-scale findings and demonstrated that SMBS is particularly effective under operating conditions characterized by elevated Pb feed grades. Laboratory-scale and plant-scale results are not directly comparable in absolute concentrate grades because of differences in feed grade, circuit configuration, operating scale, residence time, and circulating streams. During the one-week plant trial, SMBS addition to the grinding circuit reduced the average Pb grade of the antimony concentrate from 3.58% to 1.45%, despite the higher Pb grade in the plant feed during the SMBS application period. Meanwhile, the concentrate Sb grade remained high, increasing slightly from 68.53% to 69.01%, and plant operating records indicated that Sb recovery was approximately 95%

during both the baseline reference and SMBS application periods. These results indicate that the improvement in Pb control was achieved without adversely affecting Sb concentrate quality, Sb enrichment behavior, or plant-scale Sb recovery.

Overall, the combined evaluation of laboratory and plant-scale results indicates that sodium metabisulfite is an effective and industrially applicable depressant for controlling Pb impurity in antimony flotation circuits. Compared with chromate-based depressants, SMBS presents a lower environmental risk, while compared with starch, it provides higher Sb–Pb selectivity under the tested conditions. The plant-scale results further confirmed that SMBS addition to the grinding circuit effectively reduced concentrate Pb grade under high-Pb feed conditions. This study therefore presents a practical approach to improving Pb control and concentrate quality in antimony flotation.

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