Experimental Testing of Anti-Corrosive Ferrosilicon Treatments for Dense Medium Separation of Diamond-Bearing Raw Materials

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Abstract. Experimental studies have shown that electrochemical effects and inert nitrogen gas used for mixing ferrosilicon instead of air, which contains a strong oxidant—oxygen—are indeed effective methods for reducing the corrosive effects of an aqueous medium on ferrosilicon pellets. This research determined how effective nitrogen application to the ferrosilicon pellet surface was in protecting them from corrosion as they interfaced with water systems in the process of dense medium separation.

1. Introduction

The processing facilities operated by ALROSA and mining enterprises in diamond-mining countries (Botswana, Canada, South Africa, Angola) use dense medium separation (DMS) to recover diamonds from diamond-bearing kimberlites into a rough concentrate; the efficiency of this process depends on how stable the ferrosilicon properties and the physico-chemical properties of the ferrosilicon suspension are, as well as on the process water system in use [1, 2, 3, 4].

Today’s DMS facilities of diamond-mining enterprises are equipped with modular units, ferrosilicon for which needs to be imported for a fairly high price. The process involves the oxidation and degradation of this expensive dense medium, losing it as a result and ultimately resulting in a costlier diamond recovery [5].

Experimental research and testing of a DMS process has shown that ferrosilicon is mainly lost due to oxidation that jeopardizes not only the magnetic properties, but also the strength of the ferrosilicon pellets. This intensifies the abrasion, degradation, and downsizing of ferrosilicon particles <10 μm, meaning more of them are being carried away with the liquid phase of the DMS products as well as with the magnetic separation tailings [6].
Given that ferrosilicon is expensive, and dense medium separation is an ever more common kimberlite ore processing method, reducing the loss of this material in the process is a relevant undertaking.

A promising way to address this lies in reducing the oxidation of ferrosilicon pellets so as to decrease the loss of ferrosilicon in DMS [7]. This has been done in this research by applying specifically designed changes to the physical and chemical parameters of the water medium to make ferrosilicon more corrosion-resistant; and by modifying the properties of the ferrosilicon pellet surface.

2. Subject matter of research
To solve the problem stated herein, the laboratories of the Institute of Comprehensive Exploitation of Mineral Resources, Russian Academy of Sciences, Yakutniproalmaz, and ALROSA’s Geology Research Unit, joined efforts to run a series of theoretical, experimental, pilot, and commercial studies to find how to cut ferrosilicon losses by modifying the properties of process water systems and the surfaces of ferrosilicon pellets so that their parameters be within a range where ferrosilicon will be subject to no oxidation or degradation.

The research team thus studied:
– the preparation, storage, use, and regeneration of ferrosilicon suspension in the process of dense medium separation;
– dense medium separation of diamond-bearing raw materials;
– nitrogenation of ferrosilicon pellets.

In these studies, the researchers analyzed:
– granulated and crushed ferrosilicon from a variety of manufacturers and how it behaved in the DMS process;
– mineralized recycled water circulating at diamond recovery facilities;
– the liquid phase of the ferrosilicon suspension based on the water systems under analysis;
– the properties of ferrosilicon pellets as affected by nitrogenation.

3. Research essentials
To date, ALROSA’s diamond processing factories use FS15 ferrosilicon as the dense medium in the processing of diamond ores; the commercial batches of this substance contain not only iron and silicon, but also traces of doping additives. The percentages are on average as follows: 82% iron, 16.8% silicon, 0.225% carbon, 0.135% copper, 0.51% manganese, 0.20% aluminum, 0.056% chromium, and 0.014% phosphorus.

The Central Analysis Laboratory of ALROSA’s Botuobia Exploration Company (CAL BEC) ran chemical analysis of this ferrosilicon using a MARF-002 portal X-ray fluorescence unit.

This analysis found out that the original ferrosilicon had a homogeneous distribution of its chemical elements from the center towards the periphery, meaning there were no products of the decomposition of solid solutions. Corroded ferrosilicon had more oxygen and less silicon near under the surface; the iron content was not affected. This means that as the protective silicon film degrades first, it exposes iron’s porous structure, resulting in faster corrosion. These phenomena were observed by the research team’s analysis down to 1 μm in depth.

Experimental research and the practices of the diamond recovery facilities showed each class of the process samples (classes corresponding to different segments of the DMS process) had partial loss of ferrosilicon due to oxidation and degradation of ferrosilicon grains, see Figure 1 for an electron microphotograph.
The researchers then used an experimental bench to test the adjusted parameters of the ferrosilicon suspension for their ability to save ferrosilicon pellets from the corrosive effects of the external water phase; the necessary adjustments had been found by thermodynamic analysis. The following methods were experimented with as the core techniques for modifying the properties ferrosilicon pellets:

– using a water medium for DMS that had reductive properties and a relatively low ionic strength so that the oxidative processes on the ferrosilicon pellet surface would shift towards producing magnetically susceptible magnetite films. This was done by electrochemical conditioning of the water systems involved in the DMS cycle;

– preventing ferrosilicon pellets from interfacing with the air oxygen used in the preparation, storage, and mixing of the ferrosilicon suspension. This was done by replacing oxygen-containing air with inert nitrogen gas for mixing;

– preventing ferrosilicon pellets from interfacing with the mineralized waters used in the DMS process. This was done by applying nitrogen directly to ferrosilicon pellets so as to produce a protective nanoscale film.

**Phase I** was dedicated to studying the reductive effects water systems could have on the iron compounds on the ferrosilicon pellet surface.

Given the findings of previous studies, the research team decided the most acceptable method would be to electrochemically condition water to modify the redox properties of the liquid phase.

The electrochemical method has one important advantage, namely its ability to adjust the electrochemical parameters of dispersed media without affecting their salt content, which preserves the minerals’ and the water phase’s negative electrokinetic potential when using electrochemical water conditioners, whether featuring a diaphragm or not [8].

Comparative analysis of laboratory and bench studies involving such devices found they were a good option for adding reductive properties to electrolyzed recycled water running in the DMS cycle.

The properties of this water system cause the oxidative process on the ferrosilicon pellet surface to shift towards producing magnetically susceptible magnetite films, which lowers the corrosion rate of such pellets, thus reducing the loss of the material.

Note that some papers on speeding up diamond recovery processes show the positive effects of the electrochemical conditioning of water systems in some kimberlite separation cycles, including dense medium separation [9].

However, this ferrosilicon property stabilization method has not yet found a broad use in dense medium separation due to its economic disadvantages associated with the need to treat vast amounts of highly mineralized recycled water that circulates in the DMS line.

**Phase II** proposed and tested an alternative ferrosilicon loss reduction method for diamond DMS; this method was based on preventing ferrosilicon pellets from interfacing with the air oxygen involved in the preparation, storage, and mixing of the ferrosilicon suspension.

Experimental tests were run using the DMS configuration of the Processing Facility No. 3, Mirny Division; the experiments were carried out at the following laboratories: ICEMR RAS, Yakutniproalmaz, and ALROSA’s Geology Research Unit.
The results showed that using nitrogen gas as the mixing agent had the following positive effects:

– feeding inert nitrogen gas continuously while mixing the ferrosilicon suspension over 7 days reduced the concentration of water-dissolved oxygen from 5.4 to 0.9 mg/l;

– ferrosilicon oxidation rates dropped as shown by a lesser reduction in the magnetization as induced by oxidation in water: mixing with nitrogen gas produced a magnetization of 80.5 Am$^2$/kg, cf. 64.2 Am$^2$/kg in case of air [10];

– nonmagnetic sludge particles accounted for 1.26%, cf. 4.0% in case of air mixing.

Therefore, these studies showcased the advantages of using inert nitrogen gas instead of air for the preparation, mixing, and storage of the ferrosilicon suspension; this approach lowered the corrosion rates while preserving the magnetic properties of ferrosilicon pellets.

To confirm this finding, the research team ran a series of experiments, in which they tested the surface chemistry of ferrosilicon grains sampled from ferrosilicon suspensions produced by air mixing vs nitrogen mixing.

Ferrosilicon grains were extracted from ferrosilicon samples flushed with air and nitrogen over 7 days for chemical analysis on an electron microscope at ALROSA’s GRU Lab. Figure 2 shows the electron microphotographs. These images visualize the oxidation and degradation of ferrosilicon grains in air-mixed suspension samples. No obvious traces of oxidation were found on the grain from the nitrogen-mixed suspension sample.

![Figure 2. Ferrosilicon grains, where: (a) is the original sample; (b) and (c) are grains extracted from ferrosilicon suspensions mixed with (b) air and (c) nitrogen over 7 days.](image)

Laboratory observations of the positive effects of using nitrogen gas to mix the ferrosilicon suspension during preparation and storage were further tested in the quasi-industrial and industrial DMS trials at PF3, Mirny Division, using an OXYMAT N-800 ECO nitrogen station that was producing inert nitrogen gas.

These in-situ tests showed that using nitrogen rather than air to agitate ferrosilicon reduced its loss by 2.25%/day of the total loaded ferrosilicon, meaning that using nitrogen gas is indeed an effective way to prevent the oxidation of ferrosilicon particles in the DMS processing of diamond-bearing raw materials, see Figure 3.
Figure 3. Residual ferrosilicon presence as a function of nitrogen/air aeration time.

However, this method could only be used in the preparation, storage, and mixing of the ferrosilicon suspension, making its application rather limited.

**Phase III** proposed an innovation: creating corrosion-resistant nanoscale coating by applying a nitride ceramic to ferrosilicon pellets, see Figure 3 for scanning electron microscopy.

![X-ray maps of original and nitrogenated ferrosilicon.](image)

**Figure 4.** X-ray maps of original and nitrogenated ferrosilicon.

This new nanoscale coating does not alter the original ferrosilicon properties and preserves its magnetic susceptibility and strength needed for effective regeneration; on the other hand, it effectively prevents corrosive and mechanical degradation when the iron and silicon components of a pellet interface with water media of varying aggressiveness.
Applying the coating strengthens the fractured ferrosilicon particles to further strengthen the grains mechanically. Ferrosilicon consumption is expected to drop by a factor of 1.2 to 1.5.

As of writing this paper, qualified professionals from ICEMR RAS, YakutNiproalmaz, the Institute of Metallurgy, RAS, and the Mirny Institute of Technology, North-Eastern Federal University in Yakutsk, are testing this new method.

4. Conclusions
Thus, theoretical and experimental studies presented herein found a new solution capable of reducing the loss of ferrosilicon to make dense medium separation of diamond-bearing kimberlites more efficient and cost-effective. The research team tested the effectiveness of the proposed solutions, which sought to make ferrosilicon used in DMS more corrosion-resistant by:

– utilizing the effects the alkaline products of recycled water electrolysis have on the ferrosilicon pellet surface. These effects shift the oxidative reactions towards producing a \( \text{Fe}_3\text{O}_4 \) layer on the pellet surface, whereby hydrated silicon compounds crystallize;
– improving the preservation of ferrosilicon properties when aggressive water media are used, including by using inert nitrogen gas as the flushing agent in the preparation and storage of the ferrosilicon suspension;
– strengthening ferrosilicon pellets interfacing with mineralized water systems, including by direct nitrogenation producing an anticorrosive nanoscale coating (nitride ceramics).

5. References
[1] Goryachev B E 2010 Technology of diamond-bearing ores processing (М: MISiS) 326 p
[2] Verkhoturov M V 2006 Gravity methods of enrichment. Textbook for universities (М .: MAXPress) 352 p
[3] Konnova N I, Kilin S V 2013 Theory and practice of modern separation in dense media. Modeling the results of heavy-medium enrichment (Monograph - Krasnoyarsk: Sib. Feder.Univ.) 118 p
[4] Ivannikov A L, Kongar-Syuryun C, Rybak J, Tyulyaeva Y 2019 The reuse of mining and construction waste for backfill as one of the sustainable activities. IOP Conference Series: Earth and Environmental Science 362(1) 012130
[5] Williams R A, Kelsall G H 1992 Degradation of ferrosilicon media in dense medium separation circuits Minerals Engineering vol 5 Issue 1 pp 57-77
[6] Waanders F B and Mans A 2003 Characterization of Ferrosilicon Dense Medium Separation Material Hyperfine Interactions 148/149 pp 325-329
[7] Chanturia V A, Godun K V, Zhelyabovsky Yu G and Goryachev B E 2015 State-of-the-art of the diamond industry in Russia and in the world’s top diamond-producing countries (Part 2) Gorny Zhurnal 3 pp 67-75
[8] Avdokhin V M, Chernysheva E N 2003 Reduction of ferrosilicon losses in the process of heavy-medium separation of diamond-containing raw materials Reduction of ferrosilicon losses in the process of dense media separation of diamond-containing raw materials Mining informational and analytical bulletin 4 pp 240-244
[9] Chernysheva E N 2010 Increasing the efficiency of heavy medium concentration of diamond-bearing kimberlites based on electrochemical conditioning of a ferrosilicon suspension Mining informational and analytical bulletin 2 pp 403-404
[10] Timofeev A S 2017 A mathematical model of the oxidation of ferrosilicon granules in mineralized waters Mining informational and analytical bulletin 5 Special Issue 8 pp 3-11