



A flotation-based approach to the quantification of pyrrhotite in concrete aggregates

R.A. Kleiv

NTNU Norwegian University of Science and Technology, Dept. of Geoscience and Petroleum, Trondheim, Norway



ARTICLE INFO

Keywords:

Pyrrhotite
Internal sulphate attack (ISA)
Flotation
Aggregates

ABSTRACT

Pyrrhotite-bearing aggregates are a major cause of internal sulphate attack (ISA) in concrete. The concentration of pyrrhotite is usually too low to permit direct accurate quantification. Hence, safety restrictions put on aggregates are expressed in terms of the total sulphur content. This paper outlines an analytical approach in which froth flotation is employed to produce a bulk sulphide concentrate amenable to direct quantification of pyrrhotite. The concentration of pyrrhotite in the concentrate is expected to be more than an order of magnitude higher than that of the original sample. Aided by mass balancing based on conventional sulphur analysis, a safe and more accurate estimate of the *maximal concentration of pyrrhotite in the original feed* can be obtained. This could facilitate better resource utilization. Extensive work is required to develop and optimize the specific flotation procedure in order to obtain a robust analytical protocol.

1. Introduction

Internal sulphate attack (ISA) is recognized as one of the most harmful concrete deterioration mechanisms [1–4]. ISA can be described as the formation of secondary mineral phases due to reactions between the hydration products of the cement and sulphate ions produced by oxidation of sulphide minerals present in the aggregate. The accompanying volume expansion may lead to cracking or disintegration of the concrete. Iron sulphides such as pyrite (FeS_2) and pyrrhotite (Fe_{1-x}S , $0 \leq x \leq 0.125$) are common trace minerals in many rocks and are usually the main source of sulphur in aggregates. Special attention has been given to pyrrhotite due to its highly reactive nature, and a significant proportion of ISA incidents is thought to be related to the use of pyrrhotite-bearing aggregates [2,3].

To address the risk of ISA, European Standard 12,620 [5] states that aggregates for concrete (other than air-cooled blast furnace slag) must not contain more than 1% S by mass, and that a limit of 0.1% S applies if pyrrhotite is known to be present. The expression of the latter requirement in terms of % S reflects the fact that whereas total sulphur analysis can be obtained at a relatively high accuracy (e.g. by combustion analysis or wet chemical methods [6]), accurate quantification of pyrrhotite at the concentration levels in question is rarely possible.

This paper outlines and discusses an alternative analytical approach in which conventional froth flotation [7] is employed to obtain a bulk sulphide concentrate prior to analysis, thereby concentrating pyrrhotite

to a level that would allow more accurate direct quantification by one or several analytical methods. By combining direct quantification performed on the concentrate with mass balancing (based on sulphur analysis) over the entire separation process, a safe and more accurate estimate for the maximal pyrrhotite concentration can be obtained. This could reduce the risk of ISA and facilitate better resource utilization.

2. Concept

The proposed analytical approach is shown in Fig. 1. A representative aggregates sample is ground (wet) in a laboratory mill to achieve the necessary degree of mineral liberation, and a small representative sample of the ground product is retrieved by a sample splitter. The bulk of the ground product (i.e. the flotation feed) is then conditioned with surfactants (i.e. collectors) that will adsorb selectively onto the sulphide surfaces and is subsequently subjected to froth flotation using a bench scale batch flotation cell. A sulphide concentrate is recovered from the resulting froth phase. As shown in Fig. 1, both the concentrate and tails from the initial flotation (i.e. rougher flotation) can be subjected to an additional independent flotation stage. By employing scavenger flotation, a second concentrate can be produced.

The concentrations (m/m) of total sulphur in concentrate i ($c_{S,i}$) and the flotation feed ($c_{S,0}$) are determined using the methods specified [5] and described [6] by the current standards, whereas the pyrrhotite concentration (m/m) in concentrate i ($\alpha_{p,i}$) could be determined by

E-mail address: rolf.kleiv@ntnu.no.

<https://doi.org/10.1016/j.rineng.2021.100243>

Received 30 March 2021; Received in revised form 14 June 2021; Accepted 21 June 2021

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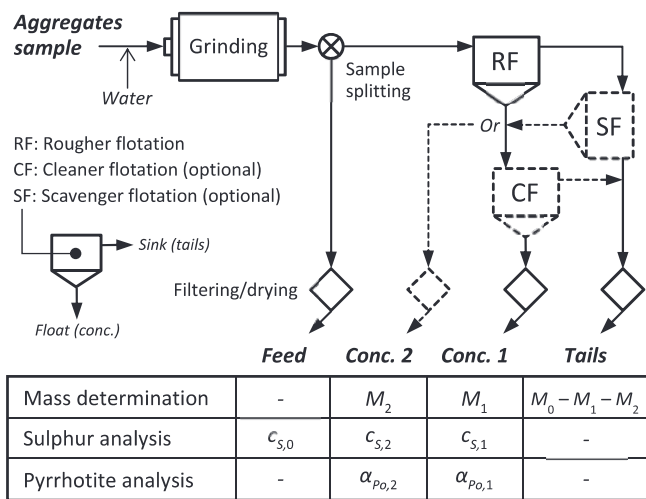


Fig. 1. Schematic representation of the proposed analytical approach. The table shows the variables determined for the respective products. Dashed lines represent optional stages and streams.

various methods as discussed further in section 3.

An estimate of the maximal concentration of pyrrhotite in the original feed sample can be found by making the precautionary assumption that the sulphur not recovered in the concentrate can be attributed entirely to pyrrhotite (assuming FeS stoichiometry) and then adding the contribution from the pyrrhotite directly quantified in the concentrate. This approach provides an estimate that always errs on the side of caution and can be expressed as:

$$\alpha_{p_o,0}^* = k \left(c_{s,0} - \sum_{i=1}^q \frac{M_i}{M_0} c_{s,i} \right) + \sum_{i=1}^q \frac{M_i}{M_0} \max(\alpha_{p_o,i}, \alpha_{p_o}^L) \quad (1)$$

where q is the number of concentrates produced (1 or 2), M_0 and M_i represent the respective mass (solids) of the flotation feed and concentrate i , $\alpha_{p_o}^L$ is the detection limit for the analytical method used to determine the pyrrhotite concentration and $k = 2.74$ is the stoichiometric mass ratio between FeS and S.

3. Discussion

The proposed concept depends on the selectivity and efficiency of the sulphide flotation process, a process that has been studied and optimized for more than a century [7–9]. Sulphides, in spite of possessing only weak natural flotability, are readily floated and separated from most non-sulphides by the use of sulphhydryl collectors such as xanthates, dithiophosphates and carbamates [9] that impart additional hydrophobicity by adsorbing selectively to the sulphide surfaces. Most sulphides, including pyrrhotite [10–13], have been subject to specific studies that have demonstrated the potential for achieving a high degree of separation [7]. Selectivity between different sulphide minerals is achieved by choice of collector(s), collector concentration, solution pH/Eh and the addition of regulating agents (i.e. depressants or activators). The same variables must be optimized to obtain a high grade/high recovery bulk sulphide concentrate and to address the challenges posed by complicating mineralogy or extensively oxidized surfaces [11,13,14]. Ideally, all the sulphides should report to the concentrate while all non-sulphides should remain in the cell (i.e. the sink fraction).

In a system employing a single flotation stage ($q = 1$) the recovery of mineral i to the concentrate can be defined and expressed as:

$$R_i \stackrel{\text{def}}{=} \frac{m_{i,1}}{m_{i,0}} = \frac{\alpha_{i,1} M_1}{\alpha_{i,0} M_0} \quad (2)$$

where $m_{i,0}$ and $m_{i,1}$, are the respective masses of mineral i in the feed and in the concentrate, whereas $\alpha_{i,0}$ and $\alpha_{i,1}$ are the corresponding concentrations (m/m). Note that Eq. (2) also expresses the overall recovery in a process where an initial rougher step is followed by a subsequent cleaner step.

The enrichment ratio for a given mineral, i.e. the ratio between its concentration in the concentrate and the feed, is defined in Eq. (3). As shown by this equation, the enrichment ratio can be expressed in terms of the mass distribution of each mineral or, ultimately, in terms of the corresponding recoveries by employing the definition given in Eq. (2):

$$\varepsilon_i \stackrel{\text{def}}{=} \frac{\alpha_{i,1}}{\alpha_{i,0}} = \frac{m_{i,1} \sum_{j=1}^n m_{j,0}}{m_{i,0} \sum_{j=1}^n m_{j,1}} = \frac{R_i}{\sum_{j=1}^n R_j \alpha_{j,0}} \quad (3)$$

If we take a simplified binary view on the mineralogy (sulphides and non-sulphides), make use of the fact that the feed concentration of non-sulphides equals $(1 - \alpha_{s,0})$ and further assume that all sulphides (s) and non-sulphides (ns) will display the same respective recoveries (i.e. R_s and R_{ns}), the sulphide enrichment ratio ε_s can be expressed as:

$$\varepsilon_s = \frac{R_s}{(R_s \alpha_{s,0} + R_{ns} (1 - \alpha_{s,0}))} \quad (4)$$

To exemplify, consider a rock sample containing exactly 0.75% pyrite and 0.25% pyrrhotite (Fe_7S_8) by weight. This corresponds to a total sulphur concentration of 0.50%, assuming that no other sources of sulphur are present. Assume that the (overall) recovery of both sulphide minerals is exactly 0.90, whereas the (overall) recovery of any non-sulphide mineral to the sulphide concentrate is exactly 0.025. The resulting sulphide concentrate will represent 3.375% of the original sample mass (flotation feed) and contain 20.0% pyrite and 6.67% pyrrhotite. The enrichment ratio for the sulphides is 26.7. Equation (1) would then yield an estimate of 0.36%, of which almost two thirds are directly quantified by the pyrrhotite analysis. Assuming an optimized protocol and favorable conditions an even higher R_s could be achieved without increasing R_{ns} , and even a very poor performance where $R_s = 0.80$ and $R_{ns} = 0.10$ would yield an enrichment ratio of 7.5.

The proposed approach does not in itself seek to distinguish between pyrite and pyrrhotite, merely to provide a concentrate that would permit the use of analytical methods that would struggle to quantify pyrrhotite in the original feed sample given the much lower concentration. Once the concentration has been increased by an order of magnitude or more, several alternative techniques (or combination of techniques) could be considered for quantifying the amount of pyrrhotite in the concentrates. X-Ray Diffraction (XRD) analysis typically has a detection limit of ~1% which makes it useless for feed analysis, but potentially useful for analysis of concentrates. The accuracy could be improved by combining XRD with stoichiometric calculation of mineral content based on chemical composition obtained from X-Ray Fluorescence (XRF) or Inductively Coupled Plasma Mass Spectroscopy (ICP-MS). In a concentrate where all the major phases have been identified and the composition of the non-sulphides are relatively low in iron, good estimates of the pyrrhotite content could be obtained from the Fe/S ratio alone. The use of Differential Thermal Analysis (DTA) or Automated Mineralogy (AM) analysis based on Scanning Electron Microscopy (SEM) would also benefit greatly from working with an enriched concentrate.

The proposed approach would not have universal applicability and would fail to offer improved estimates for materials exhibiting poor flotation performance. However, as opposed to a protocol that relies on concentration of pyrrhotite alone, producing a bulk sulphide concentrate provides an additional measure of control since both the extent of sulphide concentration and the potential amount of remaining pyrrhotite can be estimated from the more accurate sulphur analysis. Hence, the validity of the results could be tested and confirmed for each separate case and the resulting estimate would always err on the side of caution.

The accuracy and reproducibility of flotation tests depend on a large number of operational variables. This is emphasized by Wills and Finch

[8] who provide an overview of the step-by-step execution of flotation test work and the factors that must be considered. Hence, extensive work would be required to develop a robust analytical protocol. However, as opposed to flotation test work for mineral processing, the test proposed in this concept is not restricted by the fact that it also has to reflect the realistic operating conditions of an industrial process, but is free to implement any measure that would improve the degree of separation and the associated accuracy and reproducibility.

4. Conclusion

The proposed flotation-based approach can be used to provide a more accurate estimate of the total pyrrhotite concentration in an aggregates sample by concentrating the sulphides to a level that would facilitate (partial) direct quantification of pyrrhotite.

Aided by mass balancing over the separation process based on conventional sulphur analysis, the validity of the results could be tested and an estimate of the *maximal concentration of pyrrhotite in the original feed sample* can be found by making the precautionary assumption that the sulphur not recovered in the concentrate can be attributed entirely to pyrrhotite.

Extensive work is required to develop and optimize the specific flotation procedure in order to obtain a robust analytical protocol.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

References

- [1] A.P. Marcelino, J.M. Calixto, A.G. Gumieri, L.C. Caldeira, D.I. Delbem, C.M. Ferreira, A feasible evaluation protocol to determine the most reactive sulfide-

- bearing aggregate for use in concrete, *Construct. Build. Mater.* 242 (2020) 1–8, <https://doi.org/10.1016/j.conbuildmat.2020.118031>.
- [2] R. Zhong, K. Wille, Deterioration of residential concrete foundations: the role of pyrrhotite-bearing aggregate, *Cement Concr. Compos.* 94 (2018) 53–61, <https://doi.org/10.1016/j.cemconcomp.2018.08.012>.
- [3] A.A. Rodrigues, *Concrete Deterioration Due to Sulphide-Bearing Aggregates*, PhD thesis, Université Laval, Québec, Canada, 2016, 335 pages, <hdl.handle.net/20.500.11794/26812>.
- [4] I. Casanova, L. Agulló, A. Aguado, Aggregate expansivity due to sulfide oxidation – I. Reaction system and rate model, *Cement Concr. Res.* 26 (1996) 993–998, [https://doi.org/10.1016/0008-8846\(96\)00085-3](https://doi.org/10.1016/0008-8846(96)00085-3).
- [5] European Committee for Standardization, EN 12620:2002+A1: Aggregates for Concrete, European Standard, 2008.
- [6] European Committee for Standardization, EN 1744-1:2009+A1: Tests for Chemical Properties of Aggregates - Part 1: Chemical Analysis, European Standard, 2012.
- [7] D.W. Fuerstenau. A century of developments in the chemistry of flotation processing. In: Fuerstenau, M.C., et al.: *Froth Flotation: A Century of Innovation* (2007). Society for Mining, Metallurgy, and Exploration, Littleton CO, USA, pp. 3–64, ISBN-13: 978-0873352529.
- [8] B.A. Wills, J. Finch, *Wills' Mineral Processing Technology: an Introduction to the Practical Aspects of Ore Treatment and Mineral Recovery*, eighth ed., Butterworth-Heinemann, 2015, pp. 265–380. ISBN 978-0-08-097053-0.
- [9] S.J. Adkins, M.J. Pearse, The influences of collector chemistry on kinetics and selectivity in base-metal sulphide flotation, *Miner. Eng.* 5 (1992) 295–310, [https://doi.org/10.1016/0892-6875\(92\)90212-R](https://doi.org/10.1016/0892-6875(92)90212-R).
- [10] M. Becker, J. de Villiers, D. Bradshaw, The flotation of magnetic and non-magnetic pyrrhotite from selected nickel ore deposits, *Miner. Eng.* 23 (2010) 1045–1052, <https://doi.org/10.1016/j.mineng.2010.07.002>.
- [11] J. Liu, E. Li, K. Jiang, Y. Li, Y. Han, Effect of acidic activators on the flotation of oxidized pyrrhotite, *Miner. Eng.* 120 (2018) 75–79, <https://doi.org/10.1016/j.mineng.2018.02.017>.
- [12] R.S. Multani, H. Williams, B. Johnson, R. Li, K.E. Waters, The effect of superstructure on the zeta potential, xanthate adsorption, and flotation response of pyrrhotite, *Colloids Surf., A* 551 (2018) 108–116, <https://doi.org/10.1016/j.colsurfa.2018.04.057>.
- [13] J.D. Miller, J. Li, J.C. Davidtz, F. Vos, A review of pyrrhotite flotation chemistry in the processing of PGM ores, *Miner. Eng.* 18 (2005) 855–865, <https://doi.org/10.1016/j.mineng.2005.02.011>.
- [14] K.K. Brest, M.M. Henock, N. Guellord, M. Kimpiab, K.F. Kapiamba, Statistical investigation of flotation parameters for copper recovery from sulfide flotation tailings, *Results in Engineering* 9 (2021) 100207, <https://doi.org/10.1016/j.rineng.2021.100207>.