

Preface

I received an invitation from Nova Science Publishers, Inc. to contribute a chapter on a proposed book on Pyrite. Given that I have been dealing with problems caused by reactive pyrite in construction aggregates since 2007, I decided to submit an abstract. By way of response, Nova invited me to consider editing the book. While I knew this was going to entail much more time and effort than even a pessimistic estimate would predict, I agreed to take it on. The fact that I was due to retire in a few months clinched the deal. Four abstracts had already been accepted (including my own) and I was intrigued that the other three all dealt with environmentally sensitive uses for pyrite (one was since withdrawn). This was an education for me but raised some challenges with respect to technical reviews. I am pleased to state that the authors of this book represent a combination of academic researchers and practicing engineers, geologists and geoscientists. The topics covered focus on real problems and practical applications of applied research.

This book has been divided into three sections. The first section contains one chapter setting out the geological origins of sedimentary pyrite. Section two contains five chapters that provide detailed insights into the behavior of reactive pyrite and pyrrhotite when present in construction aggregates. Most recently, the consequences for property owners in Québec, Ireland and Connecticut, from iron sulfides in unbound aggregates and in aggregates in concrete have been devastating both financially and emotionally to building owners. When, through no fault of their own, their house loses some or all of its value, the impact on homeowners' lives can be shattering. The third section deals with the more positive aspects of pyrite and how emerging research is showing its value as a low-cost material for such diverse applications as coatings for solar panels and as a growth enhancer for agricultural crops.

In Chapter 1, Dan Gregory, an Assistant Professor at the University of Toronto, Department of Earth Sciences, describes the formation of pyrite in sedimentary rocks, either in the water column or in sediments during diagenesis. The main source of sulfur is from the reduction of SO_4^{2-} by sulfate reducing bacteria. He discusses the forms of pyrite and how they affect the speed of oxidation. The author then addresses the issue of trace element chemistry and how trace elements are incorporated into pyrite. It is noted that different elements incorporated in pyrite can either stabilize or destabilize the pyrite structure leading to different oxidation rates.

The issue of trace elements and their relevance to understanding the behavior of pyrite, introduced by Dan Gregory, is dealt with extensively in Chapter 3, where the concentrations of certain trace elements are used to identify the environments under which the pyrite was formed and then from that assess the propensity for oxidation. In Chapter 7, Peter Strogon addresses the formation of pyrite in sedimentary mudrocks, as well as other forms of iron sulfides in the Irish geological context.

In Chapter 2, I present the evolution of laboratory swell tests designed to simulate pyritic heave in unbound aggregate fill. I have spent 40 years as a Materials Engineering Consultant and for the past 15 years has been heavily involved as an expert in claims related to building damage from reactive pyrite and pyrrhotite in aggregates. The first swell test set-up, while failing to achieve its primary objective, nevertheless produced some unexpected results. The chapter also presents summaries of actual under slab crushed rock fill heave in a number of different buildings but all using the same aggregate source. These results allow comparison of heave rates to those obtained in the laboratory setting. Of particular interest are the results from heave monitoring over an eight-year period. The chapter concludes with an exploration of the mechanism of pyritic heave within coarse aggregate particles. Using various microscopic observation methods, the manner in which gypsum crystal growth leads to expansion provides some new insights into the damaging power of reactive pyrite.

When problems arise with sulfide-induced damage in aggregates used in construction, it seems to be on a very large scale. It is now predicted that the Irish government could pay out as much as €3.2 billion (Irish Times, 2021) in home repair costs in the northwest region of the country due to problems with mica in conjunction with pyrrhotite. These are relatively recent problems; clearly, there is still a lot to learn to prevent them happening.

Chapter 3 addresses methods of evaluating the risks for pyrite to cause expansion in unbound aggregates. The introductory section of the chapter reviews approaches taken in Québec and in Ireland and then describes an innovative application of trace element analysis to assist in such risk assessments. My colleague, Maxim Ryskin, did most of the analysis and detailed literature review on which this chapter is based. Geochemical researchers have been active in studying the origins and characteristics of pyrite in rock over the past 30 years. A key discovery of this research is that the magnitudes of enrichment of certain trace elements in sedimentary rocks is related to the environment under which the rock was originally formed. The extent to which sediments had access to oxygen and hydrogen sulfide during formation determines the forms, abundance and reactivity of the pyrite incorporated into the rock. The chapter describes and attempts to use this previous research data in conjunction with a set of trace element test data for aggregate samples from the Dublin area, including both inert and pyritic aggregates. The results show useful correlations between the concentrations of select trace elements and key factors in establishing the risk of expansion, such as total sulfur and total organic carbon. The chapter also presents some research work using the same data set to explore the possibility of using trace elements as a means to match unknown aggregate samples to the source quarry, i.e., an attempt at ‘fingerprinting’ aggregates.

Chapter 4 provides a shift in focus to pyrrhotite and the impacts when aggregates containing pyrrhotite are used in structural concrete. The chapter is authored by a research team (Josée Duchesne, Andrea Rodrigues and Benoît Fournier) at Laval University in Québec, who have led the research efforts into understanding the Trois-Rivières pyrrhotite crisis, which is estimated to have impacted 1,500 houses constructed over a 12-year period beginning in 1996. Duchesne et al. provide an expert retrospective on the causes of the severe structural damage that developed in hundreds of recently constructed houses. The aggregate source quarries are described in detail so that the microscopic origins of the problem can be understood. The chapter describes the methods of investigation and describes the development and manifestations of the damage. The manner in which the scientific findings of the investigations were used in the court proceedings are explained. The chapter ends on a positive note by describing the research initiatives undertaken to develop a performance-based test protocol to

identify problematic aggregates prior to their use in concrete. It is worth noting that this test protocol is currently being evaluated by the Canadian Standards Association with a view to adopting it as a national standard across Canada.

For those interested in learning the current state of knowledge of pyrrhotite-induced damage in concrete, Dipayan Jana's comprehensive review in Chapter 5 is a masterful treatise on the topic. As a specialist consultant in construction and geological materials, with a focus on concrete petrography and advanced laboratory investigation techniques, Mr. Jana is well qualified to provide this overview. To set the context, the chapter provides a detailed review of pyrrhotite and pyrite problems in aggregates around the world. He goes on to describe his recommended investigation techniques and the broad range of laboratory analytical techniques available for detailed examination of recovered samples. The author uses illustrated examples of how the findings of these detailed forensic examinations were used in the case of the northeastern United States pyrrhotite problems, to understand the causes and progression of the resulting concrete damage. The detailed annotated microscopic images provide excellent insights into the interpretation of the various techniques described. Based on his extensive experience, Mr. Jana provides a five-step laboratory testing protocol for assessment of pyrrhotite reactivity risk in concrete aggregates.

The combined information provided in Chapters 4 and 5 provides a comprehensive update on the current state of knowledge with respect to pyrrhotite in aggregates used in construction. At the time these aggregates were produced, there was little appreciation for the devastating impacts that pyrrhotite could cause in structural concrete. While pyrrhotite was regarded as a deleterious material, it was generally believed that the worst that could happen would be possible aggregate pop-outs or discoloration of the concrete. So, in the case of the St. Boniface quarries, the aggregate was not recommended for use in architectural concrete. Let's hope that the detailed information provided in Chapters 4 and 5 will avoid a future catastrophic failure of concrete due to the presence of reactive pyrrhotite.

Chapter 6 is devoted to another aspect of potential problems from rock containing oxidizable sulfides, especially pyrite, and that is acid rock drainage or ARD. The chapter is authored by Fred Shrimmer who has had a long career as a resource geoscientist and petrographer. He provides services to international mining and quarry operator clients as well as on civil infrastructure projects. ARD is mainly considered a problem of the mining sector where it has long been recognized as a problem due to the generation of harmful acidic leachate from waste rock piles. However, as Fred points out, transportation agencies have seen examples of ARD from roadworks arising from rock cuts, from rock tunnel work or from imported aggregates. To avoid the problem of rust-stained leachate in roadside ditches along with the environmental impacts on fish habitat and vegetation, some agencies have introduced screening protocols to identify potential ARD problems in advance of construction. Fred provides three case studies involving road projects where geological investigations were undertaken to assess risk. In this way, the need for mitigation measures can be implemented in advance and so avoid delays in the construction.

In the field of geological assessments of construction aggregates, experience is all important. On that score it is hard to compete with Peter Strogen who spent a long and illustrious career teaching Mineralogy and Petrology at University College Dublin, while at the same time earning a reputation as a practical quarry consultant as he assisted numerous operating quarries in Ireland to optimize the quality of their aggregate products. Fortunately, he is now retired and so had time to prepare Chapter 7, providing his insights into the role of

the geologist in avoiding sulfide problems, with a focus on the Irish experience. Peter provides a good introduction into sulfides in rock that complements what we learned in Chapter 1. He provides insights into the factors that influence the reactivity of pyrite. He then provides an excellent overview of the geological background to the Irish pyrite crisis. Peter expresses his views on the current technical standards for aggregates and their role in preventing aggregates containing reactive pyrite getting into construction. He stresses the importance of petrography in identifying lithologies that, although they may contain some disseminated pyrite, will not cause heave when used as aggregate.

After dealing with the havoc that sulfides can cause when present in construction aggregates, Part 3 of this book deals with pyrite from a more positive perspective. Chapters 8 and 9 present environmentally acceptable applications for pyrite as a low cost film for manufacturing solar cells and as an aid to improving agricultural productivity. These are all promising technologies that are described in some detail. Chapter 10 is a best practices overview for practitioners in the aggregate industry on how to avoid sulfides becoming another headline story for all the wrong reasons.

Chapter 8 is authored by Beya Ouertani, an Assistant Professor of Physics and Renewable Energy at the University of Carthage, Tunisia. She is also an associated researcher at the Laboratory of Photovoltaic Research and Technology Center of Energy (CRTen). The focus of her chapter is the development of techniques to utilize low cost pyrite in the manufacture of photovoltaic cells. With the continued rise in the demand for renewable energy, this line of research is welcome. The chapter takes an experimental approach to the topic by describing the process of producing pyrite thin films and then putting them through a rigorous set of tests to establish performance indicators. The first part deals with pyrite thin films with no additives. While the results are promising, the band gap energy fails to achieve the desired minimum for photovoltaic applications.

The author then introduces selenium as an enhancement to the use of pyrite alone. The process involves the selenization of amorphous iron oxide thin films, pre-deposited on glass substrates by a spray pyrolysis technique. After describing the laboratory production process in detail, the author presents the results of extensive testing on the thin films produced. Again, the fabricated thin films fail to meet the minimum band gap energy requirements. The second part of the chapter deals with alloying pyrite with ruthenium to improve its properties with respect to photovoltaic applications. The improved thin films are prepared and tested. The results confirm that pyrite prepared in a selenized atmosphere, and alloyed with ruthenium, produces thin films that have excellent performance characteristics when used in a solar cell application. A recent article in PV Magazine (Hutchins, 2020) provides an assessment of iron pyrite as a replacement for costly silica in the manufacture of the next generation of solar cells. They quoted a research group at the University of Upsala as stating that, "FeS₂ offers possibilities of the lowest-priced electricity production among the known solar cell materials". The current barrier to greater utilization seems to be low voltage performance.

Chapter 9 is devoted to an important topic, that is improving the yield of vital agricultural crops and doing it in a sustainable way. The author is Chinmaya Kumar Das from the Orissa University of Agriculture and Technology in Bhubaneswar, India. Chinmaya reviews the properties of pyrite that make it a suitable candidate for enhancing crop growth. He points out that the "Green Revolution" achieved some degree of self-sufficiency in food production by using intensive agricultural practices, such as the use of high yielding varieties and agrochemicals. However, unfortunately, these practices had some negative consequences, such

as loss of soil fertility, genetic erosion of biodiversity and ecological imbalances over a period of time. Recent research has shown that pyrite can potentially play an effective role in addressing the challenges associated with sustainable food production, by reducing fertilizer consumption, maintaining soil health and helping to retain genetic biodiversity. The chapter goes on to report the results of growing trials to demonstrate the wide range of crop types that are improved by various pre-treatments involving pyrite. These involve cereals, pulses, oilseed, vegetables, spice, flower and fodder. The author notes the major challenges that the world is facing today and suggests that the development of affordable green interventions using inexpensive earth resources can help in addressing such problems. Pyrite fits well into that category.

The final chapter contribution is from Fred Shrimmer. Over his career he has seen good and bad practices and has provided informed expert advice to solve and avoid problems. His approach complements the words of wisdom from Peter Strogen in Chapter 7. Based on his experience, Fred presents a chapter on how to avoid sulfide problems in rock products used in construction. This chapter has been included in Part 3 of the book because it addresses the positive aspects of rock utilization, despite the potential pitfalls of deleterious materials. The chapter reviews how the previous use of aggregates with excess reactive pyrite or pyrrhotite has occurred and follows up with a section on how these disasters can be avoided. The chapter makes a strong case for the use of petrography, since it is the only way to establish the types of sulfides present, their form and distribution. This is a presentation on best practices with respect to evaluating rock sources for suitability to supply construction needs. In addition to gathering the detailed subsurface information from a site investigation, the appropriate testing program needs to be used and interpreted correctly to provide the potential quarry operator with the information to operate the quarry to avoid future claims for the supply of materials unfit for purpose.

It is hoped that this book provides some new insights into a better understanding of why the presence of pyrite and pyrrhotite in construction aggregates can give rise to devastating performance problems in buildings where they are used as structural fills or as aggregates in concrete. The focus of many of the chapters is how to identify and quantify future risks so that these problematic aggregates can be avoided in future. Given that pyrite is an abundant mineral in the earth's crust, it is encouraging to see researchers working to find environmentally safe applications for it, such as for the manufacture of low cost solar panels and as a growth enhancer for essential food crops.

I would like to sincerely thank all the authors who contributed to this book. The expertise and knowledge displayed and shared is extraordinary. This book covers a broad spectrum of topics, so hopefully there will be something new for readers and researchers, irrespective of your specific research interests.

*Michael L. J. Maher, PhD
WSP Golder
Whitby, Canada
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