Interactions between dolomite and acid mine drainage in the Witwatersrand – Results of field and laboratory studies and the implications for natural attenuation in the West Rand Goldfield

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Abstract Since 2002, acid mine drainage (AMD) has discharged from the West Rand Goldfield of the Witwatersrand into nearby streams and through subsurface flow into the adjacent dolomitic aquifer. Surface discharge has also been shown to recharge the dolomitic aquifer. This has led to fears of increased dissolution of the dolomite which, it has been proposed, could lead to land subsidence in the affected area. Laboratory investigations show that precipitation of resistant mineral coatings on reactive carbonate surfaces limit the potential for dissolution of dolomite and the potential for natural attenuation.

Keywords Acid mine drainage, natural attenuation, precipitation, laboratory simulation

Introduction

Gold has been mined in South Africa's West Rand Gold Field since the late 19th Century. The gold occurs in conglomerate layers within an Achaean volcano-sedimentary basin, overlain by dolomites of the Proterozoic Transvaal Supergroup (Toens and Griffiths 1964). The mineralised conglomerates contain appreciable quantities of pyrite, leading to the generation of acid mine drainage when these are disturbed by mining (Coetzee *et al.* 2005). Fig. 1 shows the spatial relationship of the West, Central and East Rand Gold Fields to the outcrop of the Malmani Dolomite.

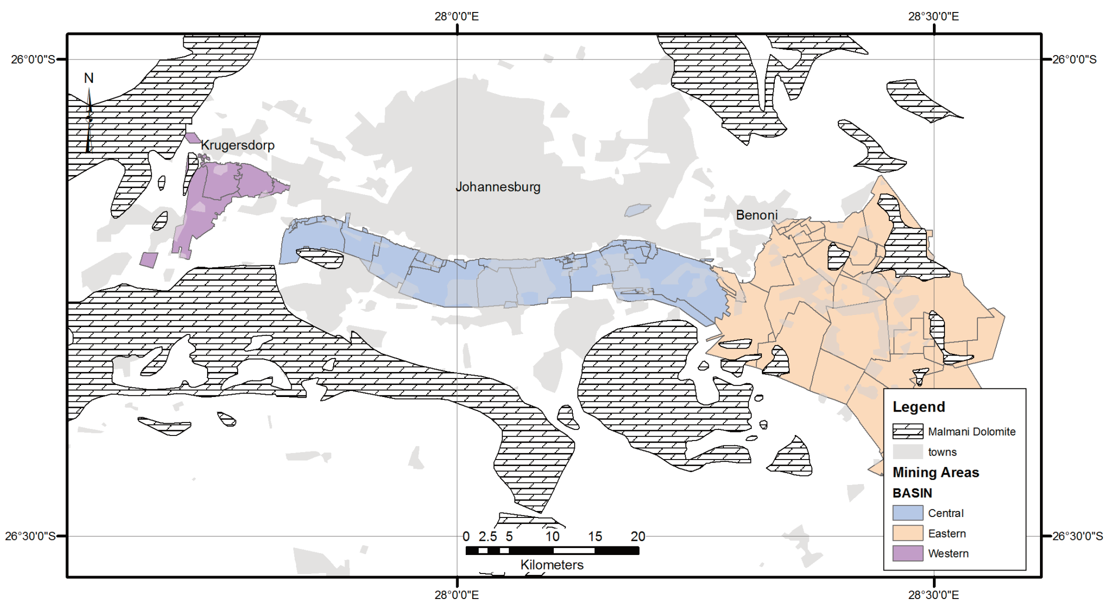

Fig. 1 *Location of the West, Central and East Rand Goldfields relative to the City of Johannesburg and surrounding urban areas and the outcrop of the Malmani Dolomite (Ramontja et al. 2011).*

Concern has been expressed relating to the possibility of acid mine drainage generated in the Witwatersrand contaminating valuable groundwater resources contained within the dolomite (Hobbs and Cobbing 2007), while Krige (2006) proposes that acidic water entering dolomitic aquifers could lead to accelerated dissolution of dolomite and the formation of sinkholes. Krige's (2006) study identifies the possibility of iron and sulphate-rich precipitates forming in the reactions between dolomite and both AMD and sulphuric acid and uses results derived from consideration of the reaction with HCl, as would be used in an acid base accounting test (Sobek *et al.* 1978), to determine the potential dissolution of dolomite. This study aims to examine the potential impacts of acid mine drainage from the Witwatersrand entering the groundwater in the adjacent dolomitic areas.

Experimental studies

Initial batch experiment

Shortly after the discharge of acid mine drainage commenced in the West Rand in 2002, a qualitative experiment was undertaken to assess the potential use of dolomite in the neutralisation of AMD. Dolomite chips were added to a sample of AMD from the West Rand and shaken overnight. This was found to only slightly raise the pH, while an orange precipitate was observed on the surface of the dolomite. This was not pursued further as it was assumed that the iron in the AMD was precipitating as a hydroxide mineral and armouring the dolomite surface, preventing neutralisation reactions from taking place.

Batch study with petrographic and mineralogical investigation

Polished thin sections were cut from a dolomite sample and investigated petrographically. Following the initial investigation, these were exposed to AMD from a shaft where water decants from the old Randfontein Estates Gold Mine. The thin sections were placed in beakers which were then filled to the brim with AMD from the shaft and sealed in an attempt to avoid additional oxygen entering the beakers. These were returned to the laboratory and agitated slowly for a period of one week to allow constant flow of AMD over the dolomite surface. Following the week of immersion in AMD the thin sections were removed and air dried to allow re-investigation to determine the effects of AMD exposure. The pre- and post-leaching chemical parameters of the AMD are presented on Table 1.

These results indicate a drop in pH during the week of leaching, most likely due to the oxidation of Fe^{2+} to Fe^{3+} with the concomitant lowering of pH, characteristic of acid mine drainage from this mine (Coetzee *et al.* 2007). This was also indicated by the precipitation of Fe^{3+} hydroxide phases observed on the samples. No neutralisation effects are seen in these data however this could be expected due to the extremely small volume of dolomite contained in a single thin section.

Petrographic investigation (Roelofse 2010) shows an exaggeration of grain boundaries and microfractures within the dolomite (Fig. 2). In some cases and the deposition of a brown coloured opaque precipitate can be seen along grain boundaries. These effects suggest etch-

Sample	pH-Initial	EC-Initial (mS/m)	ORP - Initial (mV)	pH-Post Leaching	EC-Post Leaching (mS/m)	ORP Post-Leaching (mV)
Dolomite (a)	5.44	548	-57	4.405	514	113
Dolomite (b)	5.44	548	-57	4.312	510	110
Blank (a)	5.44	548	-57	4.498	517	85
Blank (b)	5.44	548	-57	3.898	558	119

Table 1 *Chemical parameters of AMD pre and post leaching of dolomite thin sections*

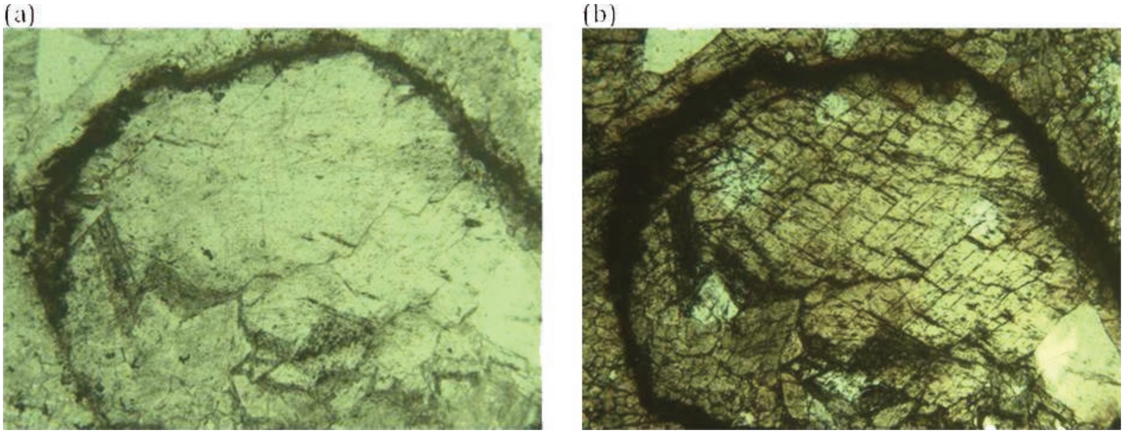

Fig. 2 *Photomicrographs (PPL) of dolomite before (a) and after (b) leaching with AMD collected the West Rand Gold Field (the dark line in the images is a line scribed in the polished thin section to allow the identification of the same area before and after leaching).*

ing of the dolomite surface by partial dissolution of the dolomite as well as the precipitation of new minerals, presumably iron hydroxide minerals, in the etched areas.

The precipitate identified on the samples was further investigated by scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) on the same polished thin sections and on crushed dolomite exposed to the same AMD as the polished thin sections, allowing the identification of the mineral precipitates formed (Fig. 3).

The precipitates formed were shown to comprise largely gypsum ($CaSO_4$) and goethite ($FeO(OH)$), which are the products expected to form due to the neutralisation of typical acid mine drainage by a calcium-rich carbonate mineral.

Column tests using synthetic AMD

Following the batch tests, a column test was designed to simulate the flow of acid mine drainage through a dolomitic aquifer. A synthetic acid mine drainage mixture (Coetzee *et al.* 2011)was prepared which aimed to simulate acid mine drainage sampled from the West Rand Goldfield, with the chemistry modified to allow iron to remain in solution to avoid rapid armoring of the dolomite with iron minerals. This was allowed to flow through vertical columns packed with different size fractions of dolomite at a constant liquid to solid ratio of around 0.1 L/kg/d. This experiment was allowed to run for a period of 5 months, with frequent measurements of pH and EC and monthly chemical analyses of the produced leachate. The results are summarised in Table 2.

During the course of this experiment, a precipitate consisting of a mixture of a white and and orange coloured mineral began to

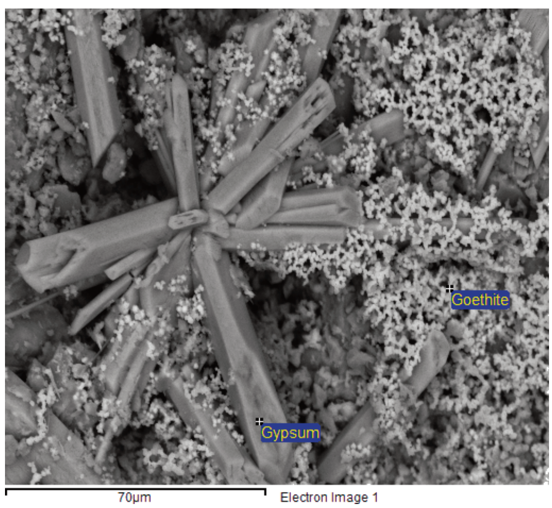

Fig. 3 *Typical SEM image of the precipitate phases in the leached dolomite samples*

Analyte	Input solution range	Column leachate range	Comments
pH	3.6	7.5-8.5	Dolomite proved effective at neutralising the synthetic AMD solution during the period of the experiment.
Fe (mg/l)	1.5-13	<0.05	Iron was precipitated during the course of the experiment.
Al (mg/l)	16-21	<0.025-0.5	Aluminum was strongly attenuated by the interactions with dolomite.
SO_4	730-920	630-920	Sulphate was hardly attenuated in the interactions with dolomite.
Ca	8-21	60-100	Calcium was dissolved from the dolomite during the experiment.
Mg	65-77	94-131	Some magnesium was dissolved.

***Table 2** Summary of the results of the column test using synthetic AMD*

form at the bottom of each of the columns (Fig. 4). SEM investigation of this material, using EDS, shows the development of a crystalline and amorphous (botryoidal) mineral containing Al, O and S (Fig. 5).

***Fig. 4** Precipitate forming at the bottom of a column due to the reaction between synthetic AMD and dolomite.*

These results illustrate the ability of dolomite to neutralise AMD. However it was felt that the low iron content of the synthetic AMD used was not realistic and that a more realistic experiment using AMD generated in the lab via the reaction of the relevant sulphidic rock material, oxygen and water would produce more realistic results.

Column test using lab-generated AMD

In order to produce a more realistic simulation of the reaction between dolomite and acid

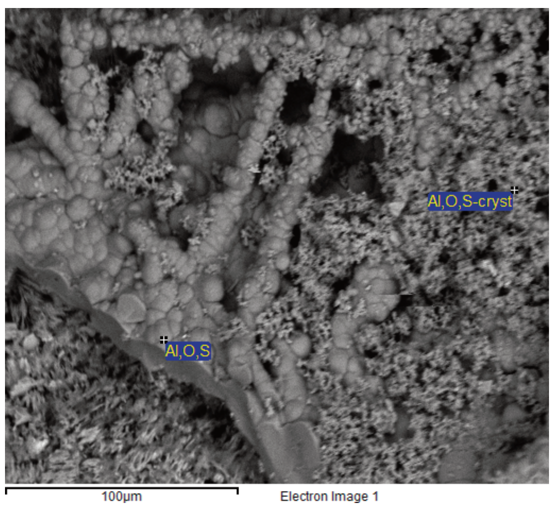

***Fig. 5** SEM image o the amorphous and crystalline precipitate generated in the reaction between synthetic AMD and dolomite.*

mine drainage for the West Rand Gold Field, a similar kinetic experiment was initiated, replacing the synthetic AMD solution with leachate generated in a column where Witwatersrand ore is exposed to water and oxygen, generating an acidic solution, as described by Tlowana *et al.* (2013). This method typically produces a leachate with an iron concentration of the order of 20-200 mg/L which is similar to measured values from the West Rand. In this experiment, neutralization was less effective and a red, iron rich precipitate formed rapidly (Fig. 6). In physical appearance, this is similar to precipitates observed in the field where AMD reacts with dolomitic material on the surface.

Fig. 6 *Iron-rich precipitate in a dolomite-filled column fed with lab-generated AMD*

Conclusions

This study used a series of laboratory experiments to assess the potential impact of acid mine drainage from the West Rand Gold Field flowing into dolomitic aquifers. Batch and kinetic experiments were undertaken and the resulting reactions characterised via analysis of the produced solutions and mineralogical investigation of the precipitates generated. The generation of precipitates on reactive dolomite surfaces will tend to armour the dolomite and prevent further reactions from taking place, potentially mitigating the risk that interactions between AMD and dolomite will lead to an increased risk of sinkhole formation. This will also stop beneficial reactions between dolomite and groundwater from occurring. This could also limit the potential of natural attenuation of AMD using locally occurring dolomitic material.

This work has been limited to the laboratory investigation of a conceptual geochemical model. The experimental studies undertaken in this study emphasise the importance of realistic laboratory simulations of natural systems. Experimental methods which aimed to limit the potential of AMD to coat reactive rock surfaces with precipitates tended to overestimate the risk of sinkhole formation and the potential of dolomite to neutralise AMD.

Field measurements to determine the range of pH and redox conditions and rock and solute compositions will be required to identify the specific reactions which are likely in different parts of the affected area. This will also require a good understanding of the local hydrogeology. Sampling of rocks and precipitates would also assist in determining which reactions have taken place.

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