THE ACIDITY OF MINE WATERS.

By F. W. Watson, B.Sc., F.I.C., and
R. A. Cooper.

The neutralisation of circulating underground waters has been discussed frequently, but as the fundamental chemical principles involved in the operation are still either unknown to or ignored by responsible persons, and serious damage thereby caused, it may be not untimely to bring the matter forward again.

In the September, 1913, *Journal* of this Society there appeared an excellent paper on this subject by Dr. J. Moir, who confined himself largely to the study of different indicators. He advised the use of methyl orange as indicating waters sufficiently neutralised to avoid corrosion. With the advent of high speed and high pressure pumps this point has been found to be highly unsatisfactory, and waters neutralised beyond it have still corroded Sulzer pumps with amazing rapidity.

A later paper was read before the S.A. Institution of Engineers by Messrs. Wartenweiler and Croghan in October, 1919. Their paper dealt principally with the mechanical aspects of the subject, such as rates of precipitate settlement and volumes of precipitate formed, and they also considered the comparative costs and efficiencies of sodium carbonate, calcium carbonate and burnt lime.

As the present paper is dealing entirely with the chemical side of the question, we will consider only the action of lime, this being the reagent most largely used. In passing, however, it may be noted that with the use of calcium carbonate there is no possibility of alternating caustic alkalinity and acidity, the effects of which are commented on later in this paper, but the neutralising action of the carbonate is slow, and only the most finely divided material is available.

Corrosion of exposed metal work in the mine will always be present to some extent, but it is greatly accelerated when acid water is in flowing contact with the metal. Active corrosive agents in mine water on the Rand may include sulphuric acid and a considerable variety of sulphates of metals, the most persistent of the latter being iron, aluminium, manganese and nickel sulphates. Other acids or their salts are not normally present except sodium chloride in small quantity. It is the behaviour of these various sulphates during the course of neutralisation that is most often misunderstood. The term " free acid " appears to be a stumbling block to many, and is probably responsible for many errors in calculation. It is usually meant to indicate acid which is in excess of the amount required to form normal sulphates with the bases present, and an attempt to determine its amount is made by titration with a standard alkali solution using methyl-orange as indicator.

A number of complete analyses of typical corrosive mine waters have been made, and they invariably show that instead of there being any excess of sulphuric acid present there is a marked deficiency of the sulphate ion below the calculated amount required to form normal sulphates with the bases present.

The following is a typical analysis (expressed as parts per 100,000):—

	Bases as Oxides Parts	SO_3 required to form normal Salts Parts
Ferrous oxide ...	3·2	3·6
Ferric oxide ...	11·4	17·1
Aluminium oxide	40·0	94·1
Nickel oxide ...	6·7	7·2
Cobalt oxide	Traces	—
Manganese oxide...	2·2	2·5
Calcium oxide ...	56·0	80·0
Magnesium oxide	36·6	73·2
Sodium oxide ...	41·1	45·4
Potassium oxide ...	1·0	0·8
Silicon oxide ...	10·8	—
Chlorine	5·2	

(= Sodium Chloride 11·1)

Sulphuric Anhydride (SO_3) 277·8 parts actually found. 323·9 parts called for.

The shortage of the SO_3 actually present below that required to form normal sulphates is 46·1 parts per 100,000.

This water could obviously contain no " free acid " in the meaning of the term as indicated above, but, on the contrary, some of the metal sulphates were present in a " basic " condition, nevertheless the water was strongly acid to methyl orange indicator.

It is therefore apparent that the designation of the acidity indicated by methyl orange as " free acid " is frequently, if not always, a misnomer.

The use of neutral copper solution has repeatedly failed to indicate the presence of any excess sulphuric acid in the most corrosive waters.

The corrosive action of such waters is due to the presence of the [H·] ion liberated by hydrolysis of the metal sulphates in solution: it is this hydrion which is the free acid of the water.

During neutralisation, metals are removed from solution in the form of precipitates, but remaining metal sulphates continually ionise and are corrosive until the neutral point is passed and all, or practically all, of the deleterious compounds have been decomposed. In the absence of any excess of sulphuric acid it therefore becomes the function of the neutralising agent to remove certain metals from solution.

A corrosive mine water containing ferric, aluminium, ferrous, nickel, manganese, magnesium and calcium sulphates was tested, and also the reactions of each individual sulphate determined.

1. Ferric sulphate alone of the above, turns methyl orange to the red colour indicating acidity, and it is also acid to all the common indicators. On the gradual addition of lime to the water the ferric iron was precipitated from solution when the original hydrogen ion concentration had been reduced from the original [H·] 1 × 10^{-2} to [H·] 1 × $10^{-3.4}$ or approximately from an acidity equivalent to $\frac{N}{100}$ to $\frac{N}{[illegible]}$ hydrochloric acid. The water was then neutral to methyl orange but acid to methyl red, phenolphthalein, rosolic acid, etc. The ferric sulphate percentage can be quite closely determined in weak solutions of the normal sulphate by titrating with sodium hydrate, taking the first change of tint of methyl orange from pink to salmon as the end point, but this change is difficult to detect when much of the reddish brown ferric hydroxide is precipitated.

2. Aluminium sulphate, the next compound to be decomposed during neutralisation, is neutral to methyl orange, and gives the salmon tint with that indicator which slowly fades during progressive alkali additions and shows no sharp change to yellow. It is acid to methyl red and indicators of the phenolphthalein class, and can be approximately determined by titration with sodium hydrate in slightly warmed solutions using methyl red indicator. The aluminium was removed from solution in the tested water when the hydrogen ion concentration was reduced to [H·] 1 × 10^{-6}—equivalent to an acidity of about $\frac{N}{1,000,000}$ hydrochloric acid. The water was then slightly alkaline to methyl orange and neutral to methyl red, but acid to rosolic acid, bromo-thymol blue, etc.

3. During the next stage of neutralisation, ferrous sulphate and nickel sulphate are removed practically simultaneously. At this stage the point of true neutrality is just passed—the hydrogen ion concentration being approximately [H·] 1 × 10^{-9} equivalent to $\frac{N}{100,000}$ alkali, and the water gives a faint alkaline reaction with phenolphthalein rosolic acid, and bromo-thymol blue. It appears to be necessary to carry neutralisation to this stage whenever the water is to be handled by high pressure pumps or used in the reduction works; in the first case, because any ferrous sulphate left in solution rapidly commences to oxidise and produce the highly corrosive ferric sulphate, and, in the second case, because ferrous sulphate, or even precipitated ferrous hydrate, is an active cyanicide and deoxidiser.

4. Slight further addition of lime precipitates manganese hydroxide and silicic acid and small quantities of magnesia, beyond this point magnesia alone is precipitated. When the test water was maintained at an alkalinity to phenolphthalein equivalent to 0·08 N CaO for 12 hours, the original magnesia content of 30 parts MgO per 100,000 was reduced to less than three parts.

The composition of the precipitates actually produced at each stage of the above neutralisation was as follows:—

Stages	1	2	3	4	5
Ferric oxide ...	95	2	—	—	—
Ferrous oxide ...	—	—	30	—	—
Aluminium oxide	5	96	—	—	—
Nickel oxide ...	—	1	68	—	—
Manganese oxide	—	Traces	1	5	—
Magnesium oxide	—	—	—	90	99
Silica	—	—	—	5	—

It is difficult to determine a satisfactory titration method for practical use which will safely indicate the decomposition of deleterious sulphates and at the same time not call for an excessive amount of alkali, as some indicators are destroyed by such precipitated bases as ferrous and manganese hydroxides, *e.g.*, methyl orange, the density of the precipitates in many cases obscures any change of colour, and there remains the difficulty that the magnesium sulphate is constantly decomposed by a slight excess of alkali, thus always tending to change the alkaline colours of the indicators back to an uncertain neutral tint. This last factor is often very pronounced and troublesome. Obviously the correct procedure would be to abandon dye indicators altogether and use an ionometer, but, as yet, these instruments are expensive and delicate.

Considerable experience has shown that very rapid titration with $\frac{N}{10}$ sodium hydrate using roselic acid indicator gives excellent results in practice, *the first appearance of a transient pink colour* being taken as the end point.

In the case of an extremely highly mineralised water a rough determination may be first made, and then, to a second portion of the sample, about three-quarters of the required alkali is added, the solution rapidly filtered, and an aliquot portion of the filtrate taken for final titration.

The practice of adding an excess of alkali to a sample and then filtering off the precipitate and determining the residual alkalinity of the filtrate gives very erroneous results, depending on the excess of alkali added, the temperature of the solutions, and the speed of operation, because this time-temperature-concentration factor controls the extent of decomposition of the calcium and magnesium compounds. When a mine water contains so much ferrous sulphate that the indicator is obscured or destroyed by the dark green precipitate it is often useful to add a known amount of very dilute hydrogen peroxide before titrating; a blank titration using the same quantity of peroxide in distilled water, being made to ascertain any necessary correction.

Experiments are being carried out to determine whether the use of neutral citrates, etc., to prevent the formation of any precipitate during titration is practicable. In view of the very great expense actually incurred by neglect of correct neutralisation on several mine properties recently, it is an immediate and pressing necessity that rapid and accurate methods of testing be known and used, and that clear records be kept and periodically examined by those responsible for the upkeep of metal work underground. Continuous addition of lime to a circulating mine water in the absence of any large additions of fresh water from fissures, etc., will eventually result in super-saturating the water with calcium sulphate (sulphate of lime), which crystallises out very rapidly when opportunity offers and obstructs pipe-lines and pumps.

This can be avoided economically in practice only by testing the water regularly and diluting with fresh unsaturated water when necessary, though in very urgent cases the addition of sodium carbonate to precipitate calcium carbonate from solution may be made to obtain immediate relief.

It should be noted that calcium sulphate is distinctly more soluble in slightly acid than in alkaline waters, but as corrosion proceeds very rapidly in solutions alternating between acidity and alkalinity it is necessary to maintain constant conditions one way or the other—alkalinity obviously being preferable. Such constant conditions can only be maintained by having an automatically controlled lime feeder which will hold at least 24 hours' supply of lime. The complete settlement of all precipitates formed during neutralisation is from the point of view of both the metallurgist and the engineer most safely carried out underground, because in most cases the precipitates are not only cyanicides and deoxidisers, but also they carry in suspension considerable quantities of siliceous grit, which is almost as destructive to high-speed centrifugal pumps as is acidity. Efficient settlement usually requires large reservoirs or large and easily cleaned filter beds, the former method being preferable, especially if some such reservoir as a disused stope, which can be easily closed at the bottom and fitted with sludge valves, is available.

In conclusion, we desire to thank the Rand Mines Metallurgical Department and Mr. K. L. Graham, Chief Metallurgist, for permission to publish this paper.

Mr. Andrew F. Crosse proposed a very hearty vote of thanks to the authors for their extremely interesting paper, which he would have great pleasure in studying carefully in the *Journal*.

The vote of thanks was seconded by Mr. Jas. Gray.

SYMPOSIUM: MINERS' PHTHISIS.

Mr. J. A. Woodburn prefaced his contribution by saying that though it had reference to the Addendum to the paper on the "Kata thermometer and its Practical Uses ing Mining,"[*] published in last month's *Journal*, the Kata-thermometer and discussion thereon were so connected with the

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[*] Original paper printed in *Journal*, November, 1920.

subjects which had been discussed in the Symposium on Miners' Phthisis, that he considered his contribution could be included under that heading.

When the original paper by Mr. Ireland was read it was stated that the Kata was quite as reliable as the average windmill anemometer used in mines, and was not liable to change of constant due to friction, etc., and was also more sensitive to low velocities, and the impression was made that it would be a more convenient and reliable instrument than the anemometer for estimating velocities in Rand Mines.

Then in the reply of the author to the discussion he says: "I am very sceptical of the accuracy of readings of air currents taken with the anemometer in underground drives and workings, especially where the air is usually eddying considerably, or even back-washing in places," but he does not claim any greater accuracy for the velocity as calculated from the Kata reading.

Now, in the Addendum just published, it is stated: "The new formulae explain some anomalies between velocities computed from Kata readings and those obtained by anemometer," and the inference seems to be that the anemometer readings were more correct and, strange to say, evidently at low velocities.

If one refers to the new diagrams as compared with the original it will be seen that to give a cooling effect of 10° reading, which is the figure recommended for hard manual effort with a working temperature of, say, 75° a velocity of somewhat over 400 ft. per minute is required according to the latest diagram, whereas the original showed that this cooling effect would be produced by about 230 ft. per minute, and if you take a temperature of 80° the revised diagram shows a necessary velocity of about 750 ft. as compared with about 510 ft. per minute in the original diagram.

It would appear that the question of cooling effect must be kept entirely separate from ventilation, which should be the actual renewal of the atmosphere, and Mr. Ireland appears to indicate this when he suggests 10,000 cub. ft. of fresh air being added to 30,000 ft. of circulating air. "To get a cooling effect comparable to a velocity of 500 ft. to 800 ft. per minute, a fan would require to be practically playing direct on the person working, and this is where Mr. Gray thinks, and I agree entirely with him, that Kata readings where the air is merely being stirred up locally, while they will give some idea of the cooling effect in the working, are practically of little use as an indication of ventilation.

Although Mr. Ireland suggests various quantities of air to be in actual circulation throughout the mine, and although he seems to think the anemometer is not quite reliable, he does not state how he would measure the quantities, and this appears to me to be a most important point. In collieries, for many years past, the anemometer served a useful purpose in arriving at the actual quantity of air passing in the various sections of a mine, and important deductions have been drawn from measurements so taken, and from all the information so far gained regarding the Kata-thermometer it does not appear to be any more reliable. I therefore cannot help reiterating my remarks that until some more convenient and reliable instrument is forthcoming, the anemometer should be employed in the Rand mines much more than it is today, and comparative figures obtained of quantities circulating in the various sections of the mines and these figures kept month by month so as to show the changes which I feel sure would take place periodically.

Mr. Ireland, in speaking on the Miners' Phthisis Symposium, in the May *Journal*, says: "The physiologists in recent years have told us very definitely what is wanted, and one feels it is now up to the engineers to deliver the goods," and in my opinion the more extensive use of the anemometer in the mines will greatly assist the engineers towards that end.

Mr. John Watson gave autobiographical details showing his early and close association in the county of Durham with the family of the late J. J. Atkinson, the authority on scientific mine ventilation. He stated that he lived in Durham County for over 30 years, and is also fairly well acquainted with the Cleveland ironstone district of North Yorkshire, but does not remember a single case of miners' phthisis in Durham, Northumberland or the Cleveland district. Even in Cleveland the mines are ventilated by centrifugal fans of adequate dimensions and velocity running over the upcast shaft. For 35 years the mines of the Rand have been dependent, chiefly, for their supplies of fresh air upon the antiquated system of natural ventilation, which means that for a good many hours out of the twenty-four there is no ventilation to speak of.

Since 1886 these fields have produced up to the end of 1918 approximately

£589,000,000 sterling value in gold, but at great sacrifice of human life. Fifty-nine years ago the late J. J. Atkinson said: "The best mode of dealing with them (*i.e.*, fire-damp, choke-damp and other gases) appears to be to dilute them with very large quantities of fresh air, and to sweep them out of the mine by an energetic ventilation as fast as they are given off or generated." The speaker was strongly of opinion that if the mines of the Rand were better ventilated the use of candles might, in places, have to be given up, but that we should be troubled much less with miners' phthisis, for which the industry has now to pay large sums annually.

OCCURRENCES OF FIRE DAMP ON THE FAR EAST RAND.

By T. N. Dewar.

(*Printed in Journal, February, 1921.*)

DISCUSSION.

Mr. C. J. Gray: In order to throw further light, if possible, on the origin of the fire-damp met with on the Far East Rand, I have thought it worth while to ascertain from official records under what circumstances fire-damp has been met with elsewhere on the Rand.

According to those records, several natives were burnt, two of them fatally, by an ignition of gas on 21 level development drive, Milner Shaft, on the Simmer Deep Gold Mine on the 29th May, 1911; a shift boss and a miner were injured by an ignition when examining the same place on the 31st May, 1911, and a native was fatally burnt by an ignition in raise 3450 E.R.I. in the Cinderella Gold Mine on the 17th March, 1913. There is little doubt but that the gas concerned in those accidents was fire-damp.

In the Simmer Deep fatal accident natives had been shovelling at the drive face for some time when one of the natives who was examining the holes with a lighted candle ignited gas which probably was issuing on a fault. When the shift boss was injured he placed his light up in a cavity about two feet broad with crystalline walls. The place was 3,900 ft. below the surface.

In the Cinderella accident a surveyor's boy, who was sent up a raise which had been standing for about a week before the accident, was burnt. The raise had passed through a small dyke and the face was in broken quartzite. Inflamable gas was found after the accident to be escaping with water from two of the machine holes which were standing in the face.

On the 19th May, 1908, in the Simmer Deep Gold Mine, a sample of gas which bubbled up through a diamond drill hole 51 feet into the footwall at 12th level east of No. 8 incline was taken for analysis. The drill had just passed through a thin seam of shaly matter. The analysis by Mr. A. McA. Johnston gave:—

	Per cent by volume.
Carbon dioxide	0·4
Heavy hydrocarbon ...	Nil
Oxygen	Nil
Carbon monoxide	Nil
Methane	77·3
Hydrogen	8·4
Nitrogen	13·9
	100·0

It is also on record that in 1903 inflamable gas was encountered in the Angelo Deep Gold Mine in shales in a borehole put down from the bottom of a vertical shaft, and that the hole was blocked by lead balls forced down by the drills, but I have not yet been able to obtain authentic details of that occurrence.

The information available, and more particularly that *re* the Simmer Deep, seems to support the idea that the fire-damp originates in shales in the Witwatersrand series rather than in coal seams in overlying strata, but is not quite conclusive.

Mr. John Watson said he would like to draw the author's attention to a paper "On the Tees Salt Industry," read by Mr. T. W. Stuart to the Newcastle-on-Tyne section of the Society of Chemical Industry, Vol. VII, 1888.

On p. 662 Mr. Stuart said: "With the view of ascertaining the presence of coal, of which 5,000,000 tons are annually consumed in and near Middlesbro', Messrs. Bell Bros. continued the boring in one instance to 250 ft. below the salt, when they found gypsum, magnesian limestone, then limestone and again gypsum and rock-salt interstratified with marl, and were obliged to stop in a bed of rock salt. The presence of this magnesian limestone lent colour to the belief that the coal might be below, but when they found small beds of salt it was