Where There is no pH Meter:
Estimating the Acidity of Mine Waters by Visual Inspection

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Abstract Most experienced mine water specialists are highly adept at judging the approximate pH of a given mine water from its appearance: usually a combination of the appearance of the water itself and of accompanying precipitates (typically ochre of various hues) and / or biofilms. For all this is a well-established art, it would appear that there has been no systematic attempt to document the thought processes which lie behind the estimation of acidity on the basis of visual inspection. Drawing on a wide range of real-world examples of mine water discharges, a classification scheme is proposed which adds a degree of formality to this practice. Using colours selected from the well-known Munsell charts for soil colour identification, a simple two-step procedure is proposed which both substantiates the estimates made by experienced practitioners and will help newcomers to the field to quickly "get their eye in" as their experience with real mine water discharges grows.

Key Words acidity, estimate, mine water, pH, visual

Introduction

After some years of field experience, most mine water specialists begin to get quite skilled at estimating the approximate pH of a given water simply on the basis of the appearance of the watercourse. This is a useful skill to acquire, as it can help focus sampling efforts on the waters with the greatest acidity and thus the highest concentrations of problematic metals. This can be particularly useful in reconnaissance work, particularly in remote areas, where heavy water bottles must be back-packed out to trailheads, often in challenging circumstances. The author knows many mine water chemists who can estimate pH to within a unit or so simply by inspection; and yet, to the author's knowledge, the basis for doing this has not previously been documented. As long as there is no codified manner of estimating pH by inspection, deductions based on it are open to challenge. For instance, in a recent dispute, a lawyer attempted to ridicule the identification of acidic waters on the basis of appearance alone: "No one can tell the pH of a water just by looking at it!" he said. Well, the author would make so bold as to claim precisely this ability, at least to within one unit on the pH scale. As the pH scale is logarithmic to the base 10, this means that visual inspection can yield an estimate of hydrogen ion activity within a single order of magnitude. Is this too bold a claim? The issue is not whether such estimates can be made: they are routinely made by practising specialists, who abundantly calibrate their observations with subsequent meter measurements and lab analyses. The issue of defensibility demands that the criteria on which pH estimates are made be explicitly defined. This paper sets out to do this. Hopefully it will not be the last word on this subject; it demands refinement by further discussion. However, it does appear to be the 'first word' in print.

Spectacular Mine Waters

Part of the attraction of mine water science is that it often deals with some of the most spectacular forms of water pollution. The spectacular nature of acidic mine drainage lies primarily in the varying colours adopted by dissolved and precipitated iron at different values of pH. Although pure aluminium precipitates tend to be uniformly white, their occurrence in mixtures with the (usually more abundant) iron deposits serves to modify the hue of the latter significantly. Finally, at the lowest values of pH certain acidophilic bacteria and algae form distinctive tendrils in acidic watercourses. It is the combination of these three visual clues which allows the estimation of pH.

Mine Water pH: A Visual Scale

Figure 1 illustrates the visual criteria on which approximate identification of pH can be made. Further explanation of the assumptions underlying the pH estimates are given below.

    The colour descriptions given in Figure 1 correspond to the formal classification scheme of

pH	Description / explanation of visual appearance.	Example photo	Locality
2	Clear water, but intensely coloured dark red (10R 3/6) due to very high concentrations (>500 mg/l) of dissolved Fe^{3+}.		Milluni, La Paz, Bolivia – floodplain filled with weathered tailings from a tin mine.
2.5	Essentially clear water (though sometimes with faint blue-green tinge, due to high concentrations of dissolved Fe^{2+}) with tendrils of green dark greenish-yellow (10Y 6/6) acidophilic microorganisms attached to the streambed.		Avoca East Adit, County Wicklow, Ireland – draining subsurface workings in a volcanogenic massive sulphide orebody.
2.5	Translucent water with high dissolved Fe^{3+} (> 500 mg/l) giving an intense red colour (10R 4/8).		Cueva de la Mora, Rio Odiel Catchment, near Huelva, Spain - flooded hollow in mine waste tips.
3	Yellowish-white (10YR 8/2) precipitates, usually of iron hydroxysulphate phases, or of mixtures of orange iron hydroxides with white aluminium hydroxide precipitates		Bowden Close, County Durham, UK. Mix of coal mine adit drainage and spoil leachate. Aluminium almost as high in concentration as iron.
4	White (N) patinas and froths of aluminium hydroxide / hydroxysulphate. These aluminium precipitates tend to become insoluble around pH 4.5.		Quaking Houses, Co Durham, UK. This is a coal mine spoil leachate with approximately equal dissolved concentrations of Fe^{2+} and Al^{3+}
5	Clear water overlying thick accumulation of yellow (2.5Y 8/8) ochre (mainly X-ray amorphous hydroxides of Fe^{3+}), drying dusky red (10R 3/4) above the water line, forming by surface-catalysed oxidation of high concentrations (~ 400 mg/l) of dissolved Fe^{2+}.		Ynysarwed, South Wales – coal mine drainage adit in the No 2 Rhondda Seam.
6	Clear water overlying moderate accumulation of light red (2.5YR 6/8) ochre, drying dark reddish brown (2.5YR 3/4) above the water line, forming by surface-catalysed oxidation of moderate concentrations (~ 40 mg/l) of dissolved Fe^{2+}.		Bardon Mill Colliery, Northumberland, UK – direct discharge from shaft drainage pipe entering the River Tyne.
7	Pale reddish yellow (7.5YR 7/5) ochre patina on rocks, formed by surface-catalysed oxidation of low concentrations (~ 5 mg/l) of dissolved Fe^{2+}.		Spittal Main Coal Drift, Berwick upon Tweed, Northumberland, UK – adit draining 100-year old coal workings on to the seashore.

Figure 1 A visual scale for estimation of approximate pH value from the colours of mine waters and their associated precipitates. Letters and figures in parentheses are approximate Munsell Colours for the features described. Note that more than one appearance can be associated with a given pH level, though all of the alternative appearances at that pH level are unique to that level

Munsell (see: www.xrite.com/top_munsell.aspx), as used worldwide in soil colour identification charts and other applications. The particular colours given in Figure 1 relate to the specific examples given, but it can be expected that other localities with similar conditions will exhibit very similar colours.

Examination of Figure 1 will swiftly reveal that there is no one criterion which can be used to estimate pH. To take the colour of precipitates, for instance: useful distinctions can be made on the basis of colour, but they need to be interpreted within the wider context of the overall field relations. It might prove possible to find dark red translucent waters in other contexts, for instance, but in a body of weathered tailings the interpretation would almost certainly be for pH 2, as shown in Figure 1. In general, however, there does seem to be a general spectrum of shades within ochre which starts at weak orange tints for neutral pH waters, reddens into the pH 5 – 6 range, then becomes more yellow through pH 4 to 3, before reddening up once more at the very lowest pHs. Quite how this relates to mineral identity is unclear, not least because XRD analyses of mine water precipitates almost always reveal very large 'amorphous humps' near the origin of the wavelength / intensity diagram, so that most of the precipitates are of indeterminate identity. We cannot, therefore, reasonably speak of contrasting colours relating to goethite, schwertmannite and haematite, even though these minerals show equilibrium relations that notionally correspond to the decrease in pH across the same range (cf Younger 1995). Furthermore, increasing proportions of aluminium hydroxide in an ochre deposit result in increasing lightness of colour.

To take another example, the tendrils of microbial material typically found in acidic waters with dissolved Fe^{2+} (suggestive of pH around 2.5, as shown in Figure 1) closely resemble those which can be observed in other settings, such as:

- A circum-neutral pH stream receiving mine water with high concentrations of zinc; as zinc is toxic to many invertebrates, zincophile algae tend to grow uninhibited in such streams (e.g. Nuttall and Younger 1999). However, it is an easy matter to recognise the non-acidic nature of such streams from the absence of tell-tale yellow and dark red ochre precipitates around the channel margins.
- Eutrophic streams strongly affected by elevated inputs of nutrients such as N and P. Normally, the absence of mining features in the landscape would rule out the (in any case rare) zincophile possibility (and biological characterisation of the microbial tendrils would swiftly confirm this), and again there would be no tell-tale signs of light ochre staining at the edges of the channel.

False friends

There is considerable scope for erroneous deduction by inexperienced practitioners. For instance, a white precipitate might well indicate aluminium hydroxide precipitation from a water with a pH around 4, as indicated in Figure 1. However, rather similar white precipitates of native sulphur can also form by rapid oxidation of previously deeply-reduced mine waters at near-neutral pH (Figure 2).

Figure 2 *Rapid precipitation of white native sulphur upon aeration of deep, anoxic, hydrogen sulphide-bearing mine waters pumped from approximately 500m depth in the flooded workings of the former Schachtanlage Robert Müser colliery, Ruhr Valley, Germany*

Figure 3 Formation of green suspended sediment of ferrous hydroxide by abrupt neutralisation of acidic mine water at Wheal Jane tine mine, Cornwall
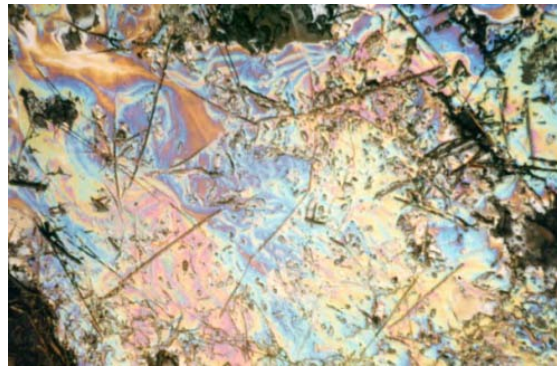

Figure 4 Newton's Colours formed by refraction of light through an iron hydroxide mono-layer formed by a colony of the bacterium Leptothrix sp. floating on the surface of acidic mine water at Shilbottle, Northumberland, UK

To give a further example, the neutralisation of previously acidic mine waters tends to give rise to large amounts of suspended solids with colours which might otherwise be associated with natural precipitates from waters at different pH values. In extreme conditions, for instance, blue-green precipitates can form by the sudden neutralisation of waters rich in Fe^{2+} (Figure 3).

Other visual signatures of mine waters can often span several pH units. In this category would be surficial mono-layers of *Leptothrix* sp., which float on the surface of mine waters oxidising iron to form black micro-crystalline solids (? goethite); these films and give rise to impressive displays of Newton's Colours (Figure 4), which are often mistaken for oil slicks by inexperienced observers.

The two are readily distinguished by simply breaking the film: oil slicks quickly re-congeal, whereas Leptothrix colonies retain broken margins. Though generally associated with acidic mine waters, these colourful films are observed across a range of pH values from less than 2 to more than 4.

Other 'false friends' relate to strongly acidic waters (pH < 2) with the same dissolved iron concentrations which range from pale green to blood red as a function of the degree of iron oxidation. Furthermore, once precipitated, iron hydroxysulphates and hydroxides can gradually change in colour as they age, even if the pH doesn't change much.

Conclusions

In essence, the estimation of pH by visual inspection is a two-step process:

- Assess the field relations, in terms of geological setting, presence or absence of mining features (past and present), and local hydrological /meteorological conditions
- Assess the colour of the water itself (especially at lower pH), of suspended particles and precipitates, and of associated biofilms (such as microbial mats in acidic waters)

Each mine water specialist should develop their skill by calibrating their observations against instrumental readings of pH, always keeping an eye out for 'false friends'.

References

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