ANDYSEZ 24
LET'S TALK ABOUT LIMESTONE - PART 1

- Andy Spate

I sometimes spend my lunchtimes reading "New Scientist" in the sunshine in a park near my office (in which I have a micro-rabbit hutch as my workspace). The edition dated 19 July 1997 has an interesting article about the contribution of the lime and cement industry to global carbon dioxide emissions and thus to global warming. More on that later. Thinking about this article suggested to me that we could profitably talk a little about limestones and what role they play in the natural and economic environment. I suppose that we can, for the moment, take the role of limestones and other carbonate rocks as contributors to the aesthetic environment for granted - after all we all gad around enjoying karst scenery above and below the surface.

Limestone is the commonest of the carbonate rocks. It is made up of the metal calcium and of the carbonate ion whose chemical formula is expressed as $CO_3^{=}$. That is one part of carbon (a solid) combined with three parts of oxygen (a gas) gets together with an ion of calcium to form the chemical compound $CaCO_3$ (= calcium carbonate). However, as I have said many times before - nothing is that simple in nature. Limestone is made up of calcium carbonate but will always be "contaminated" with all sorts of other chemical species from a variety of sources. The most usual "contaminant" of $CaCO_3$ will be the metal magnesium.

Magnesium carbonate forms the other end of a spectrum. At the limestone end we have calcium carbonate - at the other magnesium carbonate. But we do have mixtures between with differing proportions of the two metals. At the calcium carbonate end of the spectrum we call the rock limestone. At the magnesium carbonate end we call it dolomite. These two rocks have different properties - perhaps we will discuss these later.

There are lots of other contaminants. Chief amongst these will be silicates (including clay minerals), iron compounds and perhaps organic materials (including hydrocarbons). We can look at these later also if we get round to it.

These three carbonate rocks are vital to our society today.

Limestone is a sedimentary rock. But sedimentation can proceed from a number of directions - and each will produce a rock with different characters. We can have physical, chemical and biological sedimentation of limestone. However, I think that we will look at the different types of limestone and the differing depositional environments which produce limestone and dolomite in a later ANDYSEZ.

Let's talk about concrete! Now!

But, back to global warming and carbon dioxide emissions. According to "New Scientist" (19 July 1997; page 14) "cement kilns contribute more to the world's output of carbon dioxide than aircraft" (7% versus 5%) and that "CO_2 output is increasing faster [from cement and lime production] than any other industrial source". "This puts it behind power generation and vehicle exhausts but in front of aircraft". The journal goes on to state:

"Cement production creates CO_2 in two ways: by conversion of calcium carbonate to calcium oxide inside the kilns, and by burning large quantities of fossil fuels to heat the kilns to the 1450^o C necessary for roasting limestone."

We will ignore the fossil fuel question. But look at what happens when we roast limestone for cement or lime production. Lets burn one tonne of limestone - ignoring any impurities:

$$CaCO_3 + \text{heat} = CaO + CO_2$$

Note that there are the same number of ions on each side of the equation. What are the molecular weights? Calcium = 40; Oxygen = 16; Carbon = 12. Thus:

Molecular weight $CaCO_3$ = 40 + 12 + (16 x 3 = 48) = 100

Molecular weight CO_2 = 44 and molecular weight CaO = 56.

Note that the molecular weights are the same on either side of the equation - it must be working!

So if we add heat to our one tonne of limestone we produce (44/100) x 1000 kg of calcium oxide and (56/100) x 1000 kg of carbon dioxide. These difficult calculations lead to the following results:

1000 kg $CaCO_3$ (solid) + heat = 440 kg CaO (solid) + 560 kg CO_2 (gas)....WOW!

As I said this ignores impurities and is not the chemical description of cement manufacture which is more complex and consists of roasting limestone and shales (as a source of silicates) together. Rather than calcium oxide we get in this case very complex calcium silicate compounds. The carbon dioxide output also ignores the contribution from fossil or other fuels burnt to provide the heat.

According to an earlier issue of "New Scientist" (10 May) several billion tonnes of sand, crushed rock, mixtures of calcium silicate (cement) are mixed with water each year. The mixture reacts to "produce gels which then set into a rock-like mass" called concrete. Concretes continue to harden after setting as the calcium compounds react with carbon dioxide from the atmosphere. The reaction is, in fact, turning the concrete into limestone! This is a much tougher material than the original concrete. Obviously the process is very slow and it is estimated that a large slab might take 30 thousand years to carbonate fully (by which time it has probably eroded away - or been taken to the tip!).

However, someone has been doing some research to accelerate the carbonation process - and to help reduce emissions of the carbon dioxide originally produced in creating the cement. The scientist in question stated "I truly believe that...these materials [hardened concretes] will....replace steel, paper, wood and other conventional materials."

What he is doing is to bathe the concrete in $SCCO_2$ - Super Critical Carbon Dioxide. $SCCO_2$ is ordinary carbon dioxide at about 73 atmospheres (~1,000 pounds per square inch) at 31^o C. This changes the concrete back to limestone in minutes rather than millennia and produces a material with amazing properties. The compressive strength doubles and tensile strength increases by 75%; the material is tougher and develops a hard impervious outer layer which will withstand acid rain. It is suggested that the method can be used to protect old buildings and statues - but how you actually treat a building *in situ* sounds a little difficult?

It just shows you what you can do if you keep limestone in mind! And how things go round in circles. The next ANDYSEZ will talk about limestone and other carbonate rock from more geological perspectives.