Early Pyrotechnolgy

2. First Technical Uses

Birch Sap Processing

Copper axe joined to wood with birch tar

Source: Wkiepedia

- Life without a good glue is difficult. There you are, just finished with that elaborately made stone axe blade and now you need to fix it to a wooden handle. You string it on, of course, with leather or strings you made from plant fibre, but some good rubbery adhesive will keep it much better in place *and* it cushions the impacts when felling a tree or foe.
  - There are plenty of other uses for some good gummy and gluey stuff. And there is an ancient "superglue", indeed - **birch bark tar**. Don't confuse it with *birch sap*, the stuff that drips out of cut-off birch branches in the spring. Birch sap has its uses too, for example in flavoring your 4500 BC beer[1)].
    Birch bark tar is not only a good glue, you can also chew it as long as nothing better is around. And nothing much better was around when that guy (or girl), whose teeth marks where found on a piece of birch tar, chewed it about 11,000 years ago.
  - Birch bark tar has also been found on a Neanderthal spear point - with a thumb print on it. **Ötzi's** 5,300 year old copper axe was hafted with birch bark tar; the picture shows what that must have looked like.
- Birch bark tar has been used in northern Europe as a superior glue or mastic as far back as 80 000 or even 200 000 years. It never went quite out of style. The ancient Greeks used it to glue broken pots together, and the Roman Empire relied on it in a major way.
  So what is birch bark tar, and how did our remote ancestors make it?
- Birch bark tar is made by pyrolysis - the decomposition of organic stuff by heat in the absence of oxygen. All you need to do is to heat birch bark in an oven (or fire) without admitting much air. Birch bark tar boils at about 180 °C (352 °F) and thus collects as a liquid at the bottom. At room temperature it is like putty. It takes a bit of cunning to optimize the process but it is not very difficult.
  - Pure birch bark tar is not very stable when it gets wet. So you mix it with a bit of other stuff, for example red ochre dust. Ochre (an iron oxide) has been used very early as color, for example in cave paintings, and thus was well known. It makes the gum stronger and less susceptible to water, it appears. More research, however, is needed to unravel the way our remote ancestors worked with gluey things like birch bark tar or tree resins.
    Nevertheless: Birch bark tar is a product of very early *pyrotechnology*. No fire - no birch bark tar.

Wood and Stone Processing

- When you were young and read adventure stories involving savage but somehow noble warriors, they always hardened the points of their wooden spears in a fire. It never worked for me when I was a boy; I just got a spear with a burnt end. Well - you need to do it right, and some old guys knew how that worked:
  - "Pre-historic weaponmakers would rub the end of a selected wood pole against a smooth rock surface until a point was achieved. Then the point was heated in a fire, making sure to thrust the point into the coals. This put a light coating of carbon on the surface, which was then polished with a special stone, which ground fine particles of stone into the pitch which had been brought to the surface of the wood by the fire. Subsequent firings and polishings of the wooden tip of the spear would eventually form a hardened glaze consisting of pitch, wood particles and carbon on the tip which could eventually be even harder than a copper tip. This kind of primitive technology was available to primitive humans for at least 400,000 years, long before flint or stone points were used"
    I can't say it better than Wikipedia. Here we have the second example of early pyrotechnology.
- If wood gets "better" by fire treatment, how about those flintstones so important for early humans? You guessed it: roasting them a bit makes them easier to work with. Provided you do it right, of course.
  - Just throwing your chert, flint, jasper, chalcedony or whatever you like to call your "microcrystalline, cryptocrystalline and microfibrous quartz" into a fire will probably fracture those stones, due to temperature gradients and the resulting thermal stress. If you heat slowly (to avoid gradients) to (150 - 260) °C ((300 - 500) °F) and keep it there for a while (like a day or two), and then cool slowly to room temperature, you have homogenized your rocks and thus made them easier to work with. In particular "knapping", i.e. flaking of small pieces by applying pressure, is easier, and the arrow tips or whatever else is produced, were nicer and also more beautiful. On the downside, heat-treated flint was a bit softer and more prone to wear and tear.

Beautiful "Kimberley point" from heat-treated material

Source: John Webb, Marian Domanski:
"Fire and Stone" Science; Vol. 325 (2009) p. 820. Used with permission

- Heat treated flint tools are common after about 12 000 BC in Europe, before that they are scarce. In other parts of the globe, in particular Africa, the technique may be much older, though.
  - It only remains to discuss how those ancient guys, not possessing thermometers and the like, actually did it. Well, maybe like some aborigines in Australia still do it today (according to the source above). After a good fire in a pit had burnt down, the coals were removed, the bottom of the pit was covered with sand, and nodules of white chalcedony were placed on the sand and covered with some more sand. The the still glowing coals and hot sand was shoveled back into the pit and left. When the pit was cold after 3 - 4 days, the blanks were removed and worked by pressure flaking.
  - This is the third early pyrotechnology introduced in this modules. We are getting increasingly sophisticated and are now almost ready for the more complex stuff like lime burning. But first we take a break and look at something rather simple:

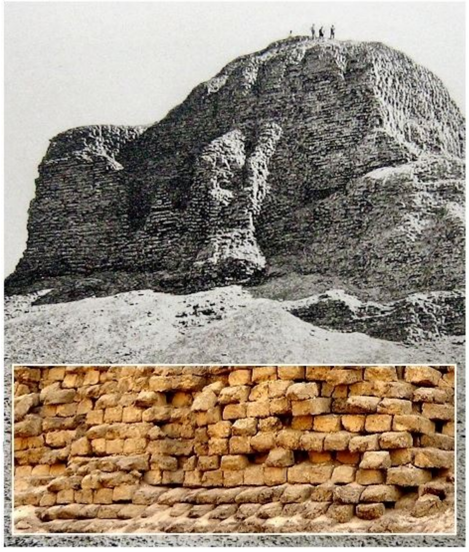
Hardening Clay

- Woman are so difficult and often hard to get. **Siegmund Freud** has put it thusly: The great question that has never been answered, and which I have not yet been able to answer, despite my thirty years of research into the feminine soul, is "What does a woman want?"'. Who knows; I certainly don't.
  Some 20 000 years back it wasn't all that different, I guess. When a guy wanted a woman, she may have had a headache or was out shopping. The thing to do was to make an effigy from whatever material was at hand, just to keep your hands busy. Then, a day after you had pitched it into the fire with disgust, you found that your little figure now was no longer soft and squeezable but hard and firm. You discovered the burning of mud in a general way.

"Fire-baked" clay figurines from Cucuteni, Dumesti (Romania), 4200 BC – 4050 BC

Source: "The lost world of old Europe" Exhibition, New York, 2010

  - There is a lot of mud out there that gets halfway solid when it dries. What is mud? "No muddy boots inside" said a sign on a school gym, followed by "Boys: mud equals dirt plus water". That is as good a definition as any I have seen.
    However, not all muds are equal. Some just decay into dust upon drying, some develop cracks, others become solid but crumbly. Nile mud with a bit of sand and straw produces sun-dried mudbricks that allow to built pyramids that last for millennia. In fact, the word " **adobe**", meaning mudbrick, derives from the Ancient Egyptian word, "dbe", with the Arabic "al" added at the beginning.



Mud-brick pyramid of Amenemhet III at Dahshur (Black Pyramid; originally 75 m tall))

Source: Internet at large

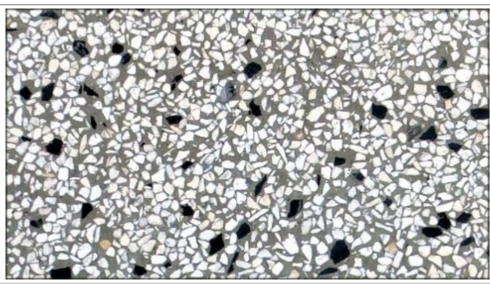
Increasing the temperature beyond what the sun can do makes for more solid bricks or figurines like the ones shown above. The oldest known piece of **ceramic**, as we call everything made from "mud" and somehow fired, is the famous Venus of Dolní Vestonice.

- However, the pyrotechnology that made those and other ceramics is not yet what one would call "*pottery*". More sophistication and higher temperatures are needed for that.

Making Lime and Terrazzo Floors

The people who lived 10 000 years ago in Göbekli Tepe, Asikli Höyük, Cayönü Tepesi or many other stone-age towns (more precisely "Pre-Pottery B neolithic) had more complex and beautiful floors in their houses than the farmers 200 years ago in the area where I live. They had polished **terrazzo floors**, sometimes even with different colors so a pattern was formed.
What is a terrazzo floor?

- A terrazzo floor consists of chips of something pretty - marble, quartz, granite - embedded in a binder like concrete or something prettier if possible. It is cast while in the semi-liquid state and then flattened, ground and polished. The trick is having a good binder or plaster.
  Pouring, flattening and polishing is comparatively easy - it's just a lot of work



Terrazzo floor in my sons's apartment building entrance.
White and black stones plus grey binder.

Portland cement would work, of course - but was something like that around 10 000 years ago? It takes a lot of energy and very high temperatures to make portland cement today, after all. Yes - but the Asikli Höyük people (and others) got rather close, as we shall see. However, if one wants to go the easy road, there are several types of plaster that are easier to make:

- *Clay* or *mud plaster*. No pyrotechnology needed. Trample it in place and watch it harden. Unfortunately, it's not water resistant. No wet cleaning there. It also wears off easily and is always dusty. I know that because that was the type of floor we (and eveybody else) had in the basements of our houses before Germany became rich.
- *Gypsum plaster*, also known as **plaster of Paris**. The white powder you mix with water to get the plaster can be made by relatively simple pyrotechnology. It is much better than clay plaster but still not fully water resistant and

rather soft.

- *Lime plaster* requires advanced pyrotechnology but forms a hard, durable, insoluble plaster with superior properties.
- *Portland cement* might be best. It actually consists of lime plaster mixed with other stuff like silicates. Nowadays it is made by heating a mixture of ingredients to about 1450 °C (2642 °F); a temperature far beyond anything possible in antiquity.

Let's look at gypsum plaster and lime plaster a bit more closely.

Gypsum plaster is made by heating gypsum or "calcium sulfate dihydrate" to less than about 150 °C (300 °F). Gypsum is a rather common mineral; you many know it as **alabaster**. Nice translucent crystals are called "**selenite**" (Greek for moon rock) even so they have nothing to do with the element selen (Se).

Natural selenite occurs in the biggest single crystals there are - in nature or in technology, just look a the picture below!

Selenite single crystals
Large picture
Cueva de los Cristales (Cave of the Crystals) in Mexico

Source: Internet at large and the "NAICA" site

What happens when you heat gypsum to rather moderate temperatures? In chemical shorthand the following:

$$CaSO_4 \cdot 2H_2O \quad \underset{(100\text{ -}150)\ °C}{\Rightarrow} \quad CaSO_4 \cdot \tfrac{1}{2}H_2O \; + \; 3/2\ H_2O$$

No need to look at details. Essentially we have a mixture of the ubiquitous molecule calcium sulfate ($CaSO_4$) and (crystal) water (H_2O). Together they form a solid with a rather complex crystal structure. That's gypsum, or to give it its proper name, calcium sulfate dihydrate. It is one of the compositions possible in the binary system calcium sulfate - water and happens to be the stable one at room temperature. We only need to consult the proper phase diagram to see what else we might get for the system $CaSO_4$ - H_2O at some temperature. Look at the phase diagram of rock salt (NaCl) and water to get an idea of what can happen in such systems.

Better even. We don't need a phase diagram. All we need is to "feel" that when we heat something containing water, chances are that we will drive out the water. That's exactly what the reaction equation above tells us. Already at temperatures somewhat below 150 °C (300 °F) most of the water goes "out" as water vapor and only a hemihydrate, called " *plaster of Paris*" remains, containing far less water (25 %, to be exact) than the untreated stuff.

If we heat to above about 200 °C (400 °F), even that last bit of water is driven out and the *anhydrate* (pure $CaSO_4$) is produced.

We won't do that, however, We just take our easily-made plaster of Paris and mix it with water at room temperature. What happens is that the equilibrium phase is formed:

$CaSO_4 \cdot ½HO + 2H_2O$	$\Rightarrow$ RT	$CaSO_4 \cdot 2H_2O$

We get gypsum back. The crystals now typically grow in the form of long interlocking needles, so what you get is a halfway nice if rather soft solid. Right after mixing plaster of Paris with water it is in a kind of pasty phase and can easily be shaped. You thus can make a nice flat floor or whatever else you have in mind.

People in the Neolithic and later, i.e. in old Egypt, did make use of gypsum for various applications. I won't dwell on it however, because most of them also had something much better:

Lime burning - the first "High Tech" pyrotechnology

The term "**lime**" is not well defined. In everyday language it refers to all calcium-containing inorganic carbonates, oxides and hydroxides; in more strict language it describes calcium oxide, i.e. CaO or quicklime and calcium hydroxide, i.e $Ca(OH)_2$ or slaked lime.On the outside it's not much different from making plaster of Paris as the basic ingredient of a paste that can be formed before it hardens. Just use ***limestone*** or calcium carbonate ($CaCO_3$) instead of gypsum / calcium sulfate for burning. Limestone is around everywhere, often mixed with some other carbonates. Burn it and you get **quicklime** or calcium oxide, CaO. Mix that with water and you get the gooey paste you are after, because **slaked lime** or calcium hydroxide ($Ca(OH)_2$) forms. It will harden slowly because it reacts with the carbon dioxide contained in the air, forming calcium carbonate and water. In chemical shorthand this writes:

Lime burning makes *quicklime*:

$$CaCO_3 \xrightarrow{(900 - 1000)\ °C} CaO + CO_2$$

Hydrating makes slaked lime:

$$CaO + H_2O \Rightarrow Ca(OH)_2$$

Carbonation hardens and makes lime:

$$Ca(OH)_2 + CO_2 \Rightarrow CaCO_3 + H_2O$$

The final process depends on the little bit of CO_2 in the air and thus is slow. The water produced makes for dampness. This is inconvenient but worth it: The final product is much harder and far more durable than gypsum. Even better, you can mix slake lime with all kinds of other stuff - from ordinary sand to that "secret" ingredients that causes the "*pozzolanic reaction*" and turn your stuff into some extremely hard and durable cement, like Portland or Roman cement - I'll get to that.
First, however, I need to look at the catch - the first law of economics applies!

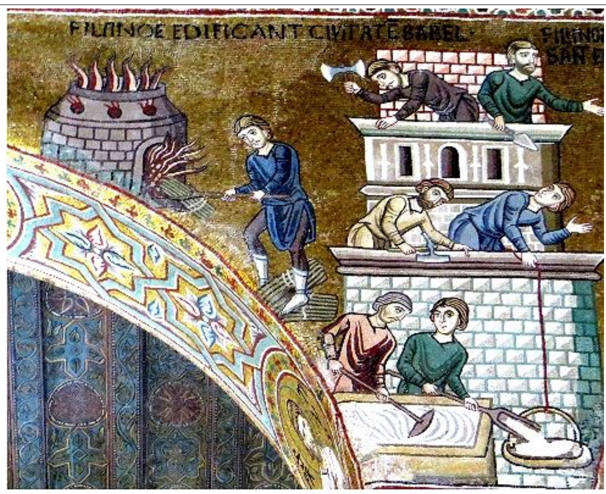
Lime burning requires very high temperatures maintained for a long time!

Pyrotechnology proper starts here. A regular fire won't do anymore. Stacking crushed limestone alternately with fuel (including some dung, perhaps) in a stone-lined pit, covering it with wood on ground level, plus piling wood or charcoal on top and containing it in a stone enclosure, would work. This has been tried, see below. Other constructions might work, too - none of them simple.

Building a working lime kiln

Source: Y. Goren and A.N. Goring-Morris: "Early Pyrotechnology in the Near East: Experimental Lime-Plaster Production at the Pre-Pottery Neolithic B Site of Kfar HaHoresh, Israel", Geoarchaeology: An International Journal, Vol. 23, No. 6, 779–798 (2008). With friendly permission.

- The capacity of the "kiln" shown above was about half a ton of limestone; needing one ton of fuel and yielding approximately 250 kg of quicklime after a burning time of about 10 hours. The maximum temperature reached was close to 900 ^{o}C (1652 ^{o}F) and thus sub-optimal.
  - In very old times lime burning might have been done as shown above. In more recent times, however, people used more complex structures. Here is one from about 1135, found as a mosaic in the Cappella Palatina in Palermo, Italy:



A lime kiln next to a construction site

Source: Mosaic in the Cappella Palatina in Palermo, Italy. Photographed 2016

- Considering that the stone-age people in Anatolia and the Levante produced copious quantities of the stuff (one floor in a large building might have used several tons), there was some speculation about those guys already cutting too much into their natural wood resources. Be that as it may, more exciting is that at least the people at Asikli Höyük mixed their quicklime with volcanic ash-particles from tuff deposits and in doing so came close to making Portland cement by the *pozzolanic reaction* [2]

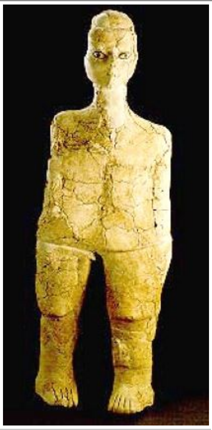
- So what the hell is a **pozzolanic reaction**? I had to look it up, too. It is the reaction between a *pozzolan* and slake lime, for example something like this:

Pozzolanic reaction		
$Ca(OH)_2 + H_4SiO_4$	⇒	$CaH_2SiO_4 \cdot 2\,H_2O$

H_4SiO_4 is obviously a *pozzolanic* material but so are many siliceous or aluminous minerals contained in the "ashes" that volcanoes coughed up, especially in the area around the town of Pozzuoli (hence the name) west of Naples, Italy.

In essence, a *pozzolanic reaction* between slake lime ($Ca(OH)_2$) and the volcanic stuff turns the *non-hydraulic* cement slakelime into an *hydraulic* cement. A *hydraulic* cement is some powdered solid that hardens if water is added, a *non-hydraulic* cement doesn't do that. Slake lime hardens if carbon dioxide is added; adding more water would just make your paste more watery. Of course, a hydraulic cement is far better than non-hydraulic slake lime. First, you don't have to wait forever before the hardening process is finished, and second, the stuff, if handled right, gets much harder and is far more durable than limestone..

- Modern hydraulic cements like Portland cement are made by mixing limestone with small quantities of other materials (such as clay), followed by burning at 1450 °C (2640 °F). That is a temperature only possible in fairly modern times. This tells us that we need to marvel at our remote ancestors, who made something coming close to Portland cement already 10 000 years ago with "primitive" stone-age technology.
  The Romans perfected the technique. Roman cement, and concrete made with it, is just as good or better than the run-of-the-mill modern stuff. The 1900 year old **Pantheon** in Rome, featuring an enormous concrete dome, is still standing. I wouldn't bet on our present concrete buildings to last that long.



Sculpture made from quicklime
Ain Ghazal, Jordan
8500 BC -5500 BC

Source: Sorry. Forgot.

While we still do not know too much about the early lime burning and terrazzo floor making technology, it is clear that the pyrotechnology involved was rather advanced both in a qualitative and quantitative sense. It wouldn't have taken much more to use it for pottery proper. Yet lime burning predates pottery by about 1000 years.

- Pre pottery B (PPB) people used their quick-lime based cements not only for making rather involved and durable terrazzo floors but also for:
  - Hafting of implements; mortar, plastering walls
  - Sculpturing faces of skulls and masks, or perhaps also for making beads for jewelry.
  - Making small sculptures like the one shown.
  - Making dishes and vessels termed "**white ware**" or "vaisselle blanche". These artifacts are sometimes considered as "pottery" items but were actually made from quick-lime without any firing.

Enough. The point is that neolithic PPB people had actually mastered pyrotechnology to a point where pottery and metal smelting would have been possible. Maybe they never "discovered" these techniques; maybe they knew them but didn't care to employ them. We will never know.

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1) Merryn Dineley: "Barley, Malt and Ale in the Neolithic" PhD Thesis. Submitted to the University of Manchester Department of Art History and Archaeology 1999. Published as a British Archaeological Report in 2004 BAR S1213

2) Andreas Hauptmann, Ünsal Yalcin: "Lime plaster, cement and the first puzzolanic reaction", Paléorient. 2000, Vol. 26 N°2. pp. 61-68.