History of Quenching

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Abstract

Iron seemeth a simple metal, but in its nature are many mysteries, and men who bend to them their minds shall, in arriving days, gather therefrom great profit, not to themselves alone but to all mankind…….attributed to Joseph Glanvill (1636–80)

The basic concept of heat-treating, and specifically quenching, is intertwined with the history of civilization. It is the efforts of these pre-industrialized people that laid the foundation for modern metallurgy, and our understanding of materials behavior. In this paper, the early history of quenching will be described from the dawn of civilization to the early industrial age. The focus will be primarily on the contributions of Europeans, Indian, Chinese and Japanese civilizations.

Introduction

Much of the history of quenching is shrouded in mystery – especially from roughly 400 BC to approximately 1500 AD. This is thought to be a result of the general education of the people, and the desire to protect intellectual property by the many blacksmiths and guilds. It was only until much later, that many of the quenchants, and the methods of quenching were described. The methods of quenching were determined through empirical research, and much experimentation. It was only until much later, after approximately 1850 AD, that the science of quantifying the effects of quenchants and alloying elements was developed. Steel hardenability, martensite formation and the mechanism of quenching would have to wait until the necessary analytical tools were developed.

Much of the history of quenching is interlaced with the early production of iron. Probably one of the earliest references to smelting and blacksmithing is from the Old Testament [1] in Genesis 4:22:

Figure 1 - Jubal and Tubalcain in the smithery. UNKNOWN; Illustrator of 'Speculum humanae salvationis', Cologne, c. 1450. Museum Meermanno Westreenianum, The Hague.

"Zillah also had a son, Tubal-Cain, who was an artificer of bronze and iron."

Interestingly, the name "Cain" is a cognate with the Arabic *qayin* "smith". The name Cainities is also the description of the Midianite tribe, which some have inferred to be the Hittites [2].

It is not known when steel was first created, or who first created steel. It is suggested from tradition (Herodotus, Xenophon and Strabo) and archaeological evidence[3][4] that iron working developed in the Middle East, in Turkey, near the plateau of Anatolia in 1400-1200 BC by the Hittites [5][6][7]. Iron smelting was well known by the second millennium, and described by Homeric poems (880 BC), the History of Herodotus (446 BC) and Aristotle [8] (350BC). Because of ore variation, and the skill of the individual craftsman, the production of steel was often poor quality, and limited in production [9].

One of the first mentions of quenching is from Homer (circa 800BC):

> *"As when a man who works as a blacksmith plunges a screaming great axe blade or adze into cold water, treating it for temper, since this is the way steel is made strong, even so Cyclops' eye sizzled about the beam of the olive…." Odyssey 9.389-9394, translation by R Lattimore*

This dramatic image of quenching indicates familiarity with the concept of quenching of steel. Much of the history of quenching has been shrouded in mystery and magic.

One of the earliest myths perpetrated regarding quenching ancient steel, was the idea that slaves or virgins were used as a quenching medium. The idea being that the hot sword or knife would be plunged into the body of a slave would impart special properties. Slaves as a quenching medium was first presented with a tounge-in-cheek by Douglas Fisher [10]. This was subsequently noted by John Sullivan [11]. From a practical perspective, it is not likely that slaves or virgins were used as a quenching medium. The physical force required to plunge a blade while hot would likely cause the blade to deflect and warp. Further, it is likely that the slaves would tend to writhe about, causing distortion to the blade. Lastly, slaves and virgins are not renewable. Any large production would certainly exceed the available supply.

In the first millennium, few technological advances were made in Europe. Some Icelandic sagas spoke of searching through many kingdoms to find the proper water to harden the sword Ekkisax and weapons that are hardened in blood. Predominately, the advances in metallurgical technology were located in the Arab World, India, China and Japan. While European armor blacksmiths were improving, and gradually perfecting their craft, the Crusaders of the 12th century had no steel that was the equal of Islamic metallurgy. The Japanese sword was even better than the Islamic sword by an even greater margin [12].

India

The primary contribution of India was the production of high quality steel called Wootz steel. The quality of the steel was excellent, and exported to Europe, China, and the Middle East. The 12th century Arab Idrisi wrote "*The Hindus excel in the manufacture of iron. It is impossible to find anything to surpass the edge from Indian steel.*"[13].

The first real production of steel on a large scale was produced in India around 500 B.C. [14]. This steel, which even in relatively modern times, was known for its high quality:

'…there is a cake which is supposed to be steel from India and the kind to be rated most highly in Egypt. I could find no artisan in Paris who succeeded in forging a tool out of it.' Rene Antoine Ferchault de Reaumur, (1722) [15]

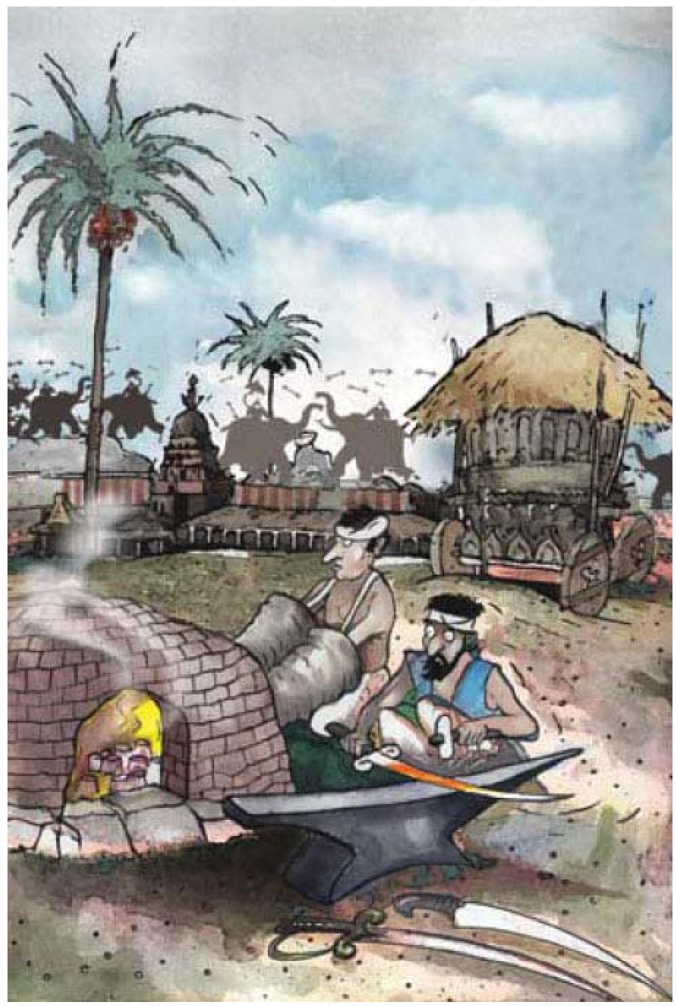

Figure 1 – Figure showing Indian blacksmiths creating swords, from the cover of "India's Legendary Wootz Steel: An Advanced Material of the Ancient World [16]

Sherby[17], describing the production of Wootz steel, indicates that wrought iron is broken into pieces in a sealed crucible, with a pre-measured amount of charcoal. The crucible is heated to approximately 1200ºC. The wrought iron absorbs the carbon, and the melting point is lowered. The process is completed when the crucible is shaken, and the sound of molten iron is heard. The crucible is slow cooled over several days. Large grains of Cementite are formed, and a homogeneous alloy of 1.5-2% carbon is formed.

These buttons are then heated to a relatively narrow range of 600º-850ºC. In this temperature range the Cementite does not completely dissolve. Upon forging or hammering, the Cementite grains are broken up, resulting in a mixed, banded microstructure, with the trademark swirl of Damascus Steels [18]. This forging technique explains the strength, toughness and ductility, and the mythology of Damascus steels, which have been produced since 330BC. This steel was exported to China, Persia, Arabia and eventually Europe.

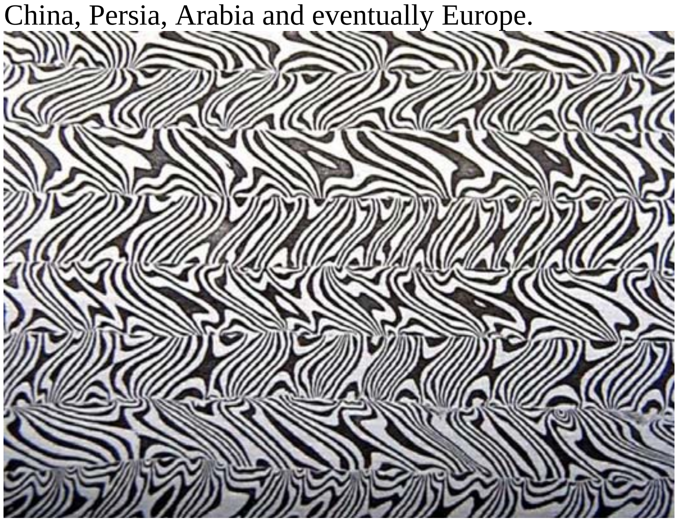

Figure 2 – Damask pattern, courtesy of Manfred Sachse.

Middle East

Not much is known of the methods of quenching in the Islamic world. It was known that the swords of the Islamic world were high quality. A writer from the Crusades, regarding the quality of Damascus blades fashioned from Wootz steel described the quality of the blade as "*One blow of a Damascus sword would cleave a European helmet without turning the edge, or cut through a silk handkerchief drawn across it.*"[19].

al-Biruni, writing in the *Kitab al-jamahir fi ma'rifat al-jawahir*, in the 11th century AD, specifies what *dawa* is in Indian practice. He writes [20] "*…in the process of quenching the sword they coat the flat of the blade (matn) with hot clay, cow dung and salt, like an ointment, and clean the two edges with two fingers….*"

This is similar to the process of making Japanese blades, and the application of *yakaba-tsuchi* clay.

The account of Second Captain Massalski, as published in *Annuaire du Journal des Mines de Russie*, 1841, says Persians quenched their Wootz steel in pre-heated hemp oil. The Captain says some smiths added a little grease and bone marrow to the quenchant.

> *"If it is a dagger it is held flat; if it is a sabre, it is quenched little by little, beginning by the end of the cutting edge, holding the latter toward the bath. This manoeuvre is repeated until the oil stops smoking, which proves that the blade has cooled. After quenching the blade is always soiled with burnt oil. This dirt is removed by heating it enough to set light to a piece of wood, and by rubbing with a rag from a bedsheet."*
>
> *English Translation by Graham Cross.*

Pretextat Lecomte is a French painter and mosaic artist who lived in the end of 19th century, and was invited to Istanbul for the restoration and reconstruction of some historical art pieces. He spent many years in Istanbul, and from his studies of oriental arts, he wrote the "Arts and Crafts of the Orient" in 1903. (*Les Arts et Metieres de la Turquie de l'Orient*, published in Paris in 1902).

He mentions that most of the Ottoman sword blades were made in Damascus (Today's Syria was a part of the Ottoman Empire during that time), and those blades had a superior steel which was made in a totally different way than Europeans:

> *"...Steel is iron, mixed with charcoal. In Damascus, 10-12 kilograms of iron was required for making one sword blade. Craftsmen mixed this ore with charcoal dust, melted it again and again, until it came to a consistency of their mind."*
>
> "...Now it was required to quench it in order to give it the necessary strength, and that was the interesting point of the procedure: Europeans quench the steel in water, vegetable oil, or cattle fat, but in the East they were doing it on air. When the craftsmen were done with the processing of the metal, they heated it until totally red, and gave it to a cavalry man waiting on his horse, ready for a ride. The cavalry man rode his horse in the wilderness, waving the blade in the air with crazy screams to make his horse ride faster."

Lecomte concludes with that although swords were still made in Damascus during his time, this craft had already disappeared for economical reasons: The swordsmiths in Damascus started using imported steel from Britain because it was much cheaper.

On the other hand, “air quenching” was certainly not the only method for making “superior steel” in the Ottoman period. Kemankes (*translation is Bowman*) Mustafa Aga gives a special formula in his book, “The Book of Arrow” [21], for making armor-piercing arrowheads and sword blades. His quenching medium consists of:

> *1 okka Quick Lime (CaO)*
> *½ okka Soda (NaCO)*
> *½ okka Carbonas Cupricus (Copper Oxide?)*
> *½ okka Arsenic Sulphate (AsS)*
> *2 okka Radish juice*
> *1 okka Wild Onion juice*
> *½ okka Valonia ash*
> *1 okka Tar*
> *(Okka is a weight unit and corresponds to 1283 grams.*)

China

The earliest known Chinese word for quench-hardening is *cui* [22] and is still used in the modern term for quenching *cuihuo* [22]. Water was predominately the preferred quenchant:

> *When a skilled metallurgical worker ‘casts’ [zhu] the material of a Gan Jiang [sword], quench-hardening [cui] its tip with pure water and grinding its edge with a whetstone from Yue, then in the water it can slice water-dragons, and on land it can cut rhinoceros hide as quickly as sweeping and sprinkling or drawing in mud.*
>
> Sheng zhu dexian chen song presented to the Emperor Xuan-di (73 BC to 49 BC) by Wang Bao [22]

There is some thought that the idea of quenching was a Han Dynasty innovation [22]. Early Tang texts indicated that the Yunnan quench-hardened steel in “the blood of a white horse”[22]. Various texts indicate that different waters were good for quenching, while others were inadequate. The Qingzhand and the Longguan Rivers were noted for being good for quenching: [22]

> *“The Han River is sluggish and weak and is not suitable for quench-hardening. The Shu River is bold and vigorous…..”*[19]

This empirical line of thinking appears to be universal. The Elder Pliny, in the 1st century, also indicated that certain waters were good for quenching. [23]

Quenching in vinegar was considered to be poor practice “making it brittle and easy to break” [22]. It is not known why this practice would be considered to be poor practice, as it should give similar performance to a brine-type quench.

It seems that quenching in urine was a common practice, with quenching in the urine of five sacrificial animals or the fat of five sacrificial animals. It was given that “such a sword could penetrate thirty layers of armor” [22].

There was also an understanding of the effects of different quenchants, and the effect on performance. In 6 AD, the blacksmith *Qiwu Huaiwen* used animal urine and animal grease to effect different quench rates. The characters used differentiated this: *cui* was denoting quenching in animal grease, while *yu* was designated for quenching in urine. *Song Yingxing* discusses quenching in oil, which provides a softer quench, “since the strength of steel lies in quenching”. Further it was noted that barbarians quench in *di son*, the “urine of the earth”, a kind of oil not produced in China [22]. This perhaps is the first possible mention of quenching in petroleum-based oils.

Japan

The metallurgical state-of-the-art was very advanced in Japan. The science and craftsmanship of the Japanese sword is still revered today for being beautiful and effective, capable of maintaining a sharp edge and the unique curve of the blade.

Swords made by the traditional method are manufactured from steel produced by the *tatara* method. This steel, or *tamahagane*, is produced from iron sands that have very low Phosphorus and Sulfur.

The basic process is similar to that practiced by the Europeans in the 5-6th century AD. The sharp edge consists of high carbon steel to retain an edge, and the interior of the blade consisting of lower carbon steel for toughness and ductility. However, the Europeans immersed the entire sword in the water, with the entire surface of the sword quenched rapidly. In the Japanese method, controlled quenching is achieved at specific rates at different locations on the blade.

Prior to heating, the Japanese sword maker applies a closely guarded secret clay mixture (called *yakiba-tsuchi*), that consists of stone powder, clay and charcoal. The stone powder helps prevent the clay from cracking during heating of the blade; the charcoal is burned out during heating, producing a site for initiation of nucleate boiling, depressing the formation of the vapor phase. The thickness of the clay determines the quench rate. The clay is thinnest at the edge of the blade, and thickest at the ridge of the blade – opposite the edge. The blade is immersed in water in the water box or *mizubune*. The edge is quenched with the highest heat transfer rate and produces martensite, while the ridge experiences a much milder quench and transforms to a mixture of pearlite and ferrite. The interface between the pearlite and martensite is called the *hamon*.

This unique and ingenuous method of quenching also produces the characteristic curvature of the blade. As the blade is quenched, the edge contracts, and reverse bending occurs, called *gyaku-sori*. At the martensite transformation, the *sori*, or normal bending occurs, due to the volumetric transformation of martensite. *Gyaku-sori* appears again at the pearlite transformation at the ridge of the blade. Finally, the final curvature or *sori* appears as the pearlite contracts due to thermal contraction, contributing to strong compressive residual stress at the blade edge. Final tempering of the blade, or *aidori*, is done in a charcoal fire. This understanding of the quenching process, practiced since the 5-6 century, shows the advanced nature of the Japanese metalsmiths.

Europe

Probably the first significant work in Medieval Europe was written by Theophilus (1125), a 12th century German Monk. The "Diver Arts" describe several good quenchants. His recommendations for quenchants were very specific:

> *"Tools are also given a harder tempering in the urine of a small, red-headed boy than in ordinary water."* [24]

Other recommendations for quenchants included the urine of goats fed ferns for three days.

Giambattista della Porta (ca. 1535-1615) in his books "Natural Magic," described the temperatures of steel to be quenched:

> *"When the iron is sparkling red hot, that it can not be hotter, that it twinkles, they call it Silver; and then it must not be quenched, for it would be consumed. But if it be of a yellow or red color, they call it Gold or Rose color; and then quenched in Liquors, it grows harder. This color requires them to quench it. But observe that if all the Iron be tempered, the colour must be blue or violet color, as the edge of a Sword, Razor, or Lancet; for observe the second colors; namely, when the iron is quenched, and so plunged in, grows hard. The last is Ash color; and after this if it be quenched, it will be the least of all made hard."*

This was a critical observation. He indicates a critical range for quenching, based on the colors of the heated steel. Only when the steel is rose or yellow will the steel be hardened properly. Further, the observation of tempering colors was indicated. As Cyril Stanley Smith[28] pointed out, it led Della Porta to realize the advantages of the two-stage quench over a direct quench, and reject some of the more exotic quenching baths that was cited in earlier metallurgical literature.

Figure 1 - Process in creating a Japanese Sword, from top to bottom: The steel is heated prior to the forging process in a charcoal fire; After hammering the steel out, it is cut in half and folded; The folded steel is then hammer welded together, as the forging process continues; The smith then continues to shape the blade, first with a power hammer and then with a hand held hammer; After forging, the blade is shaped by hand, and then coated with clay, prior to the hardening process; After the claying of the blade, it is heated to critical (about 1450°F) and then quenched in water, creating the martensite edge and pearlite body of the sword; The blade is then final shaped and polished. This sharpens the blade and reveals the hamon that is created by the hardening process. Figures courtesy Bugei Trading Company.

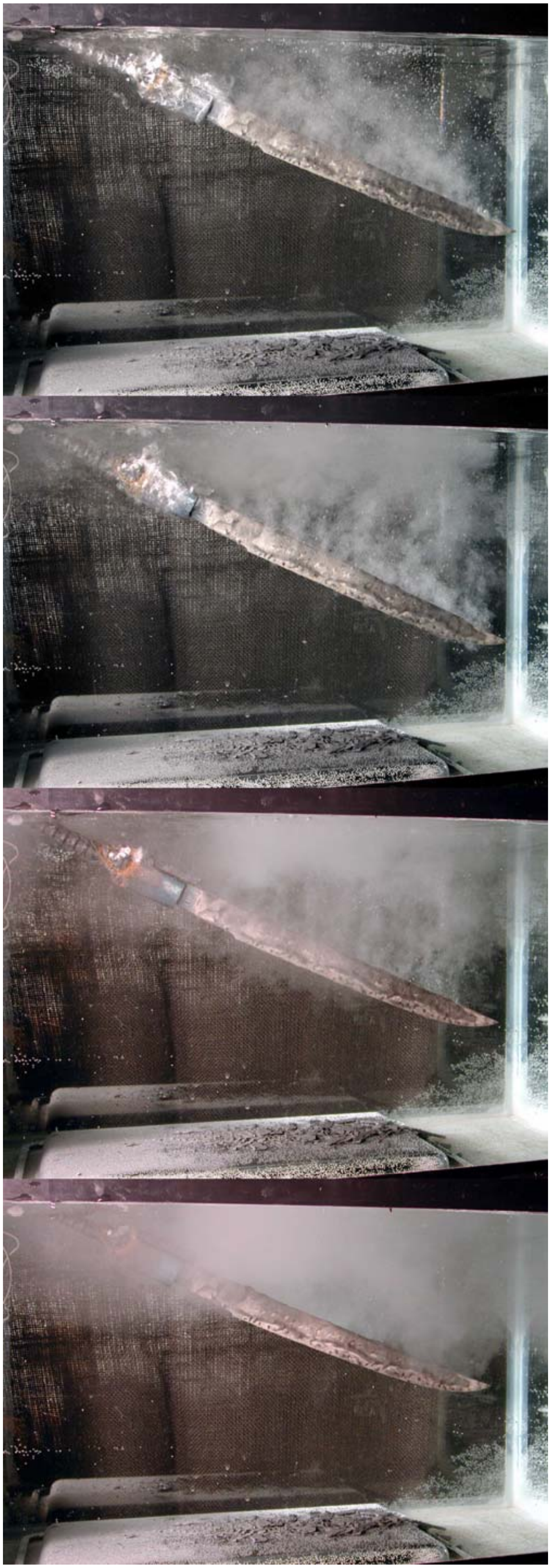

Figure 5. Sequence of quenching a Japanese Tanto: This blade was coated with clay (yakiba-tscuchi); The nose or tip of the blade (kissaki) is down showing gyaku-sori; Blade is now straight again; Nose is up as in the typical final curvature of a Japanese blade (sori). Photographs courtesy of Jesus Hernandez and Walter Sorrells.

He emphasized the necessity of using clear quenching liquids so that the tempering colors could be observed, and recommended rubbing a blade with soap before heating it, "*that it may have a better color from the fire*."

Porta was one of the first people to recognize that there were various tempers of steel, and described methods to achieve those tempers. In describing the "Temper of Files" in his Thirteenth Book of Natural Magic:

> *"…take the chest out from the coals with iron pinchers, and plunge the files into very cold water, and so they will become extremely hard. This is the usual temper for files, for we fear not if the files should be wrested by cold waters."*

Porta also showed an excellent understanding of the reason why many quenchants were effective, and some of the underlying principles:

> *"If you quench red hot iron in distilled vinegar, it will grow hard. The same will happen, if you do it into distilled urine, by reason of the salt it contains in it. If you temper it with dew, that in the month of May is found on vetches leaves, it will grow most hard. For what is collected above them, is salt, as I taught elsewhere out of Theophrastus. Vinegar, in which Salt Ammoniac is dissolved, will make a most strong temper. But if you temper Iron with Salt of Urine and Saltpeter dissolved in water, it will be very hard. Or if you powder Saltpeter and Salt Ammoniac, and shut them up in a glass vessel with a long neck, in dung, or moist places, till they resolve into water, and quench the red hot Iron in the water, you shall do better. Also Iron dipped into a Liquor of Quicklime, and Salt of Soda purified with a Sponge, will become extreme hard. All these are excellent things, and will do the work."*

There was also an understanding of the cause of quench cracking, and the results of quenching in other than water for "*The Temper for Instruments to let blood":*

> *"It is quenched in oil, and grows hard, because it is tender and subtle. For should it be quenched in water, it would be wrested and broken."*

Various authors, describe other quenchants: pigeon droppings, flour, honey, olive oil and milk [25][26][27]. Other quenchants, including urine, water and solubilized animal fats and whale oil are described by Smith [28], Biringuccio [29], Agricola [30] and others:

Figure 6. Coverplate from John Baptist Porta, "Natural Magick in 20 Bookes"

"Take clarified honey, fresh urine of a he-goat, alum, borax, olive oil, and salt; mix everything well together and quench therein."

"Take varnish, dragon's blood, horn scrapings, half as much salt, juice made from earthworms, radish juice, tallow, and vervain and quench therein. It is also very advantageous in hardening if a piece that is to be hardened is first thoroughly cleaned and well polished."

Excerpts from Von Stahel und Eysen (1532)[31]

Haedke [27] indicated that the swords and knives made in Toledo, Spain were known to be of high quality as early as the ninth century. Heat-treating occurred on a night with a warm south wind, and clouds obscured the stars. A cherry red heat was taken on the blade, and it was quenched immediately in the Tajo River.

Hanko Doebringer's writings on swordsmanship from about 1389 [32]. In the same manuscript, there are formulas for hardening, tempering, and annealing metal.

Wiltu stol herten / und gar gute sneiden machen zo nym buglossam / blateloze mit worcze und mit al und sewt das in kaldem wasser / und herte was du wilt

An approximate translation is:

"If you wish to harden steel, and make extremely good blades, then take Buglossam without the leaves, including the root, with [eels? oil?] and steep that in cold water. And use this to harden whatever you want." [Note: Buglossam is an herb, also called Porrago or Borras.]

A quench for hardening a stonemason's hammer:

Wiltu hemer herten do man steyne mete hewt / So nym rupen saff / Do lesche dy hemer gluende dorynne

"..If you wish to harden a hammer so that it can be used to cut stone, then take turnip juice, and quench the hammer in it while it is glowing.

The term *rupen saff* could also be *Rubensaft*, which could be turnip juice, beet juice, or rapeseed juice. Rapeseed oil is commonly used as a lubricant for machines, so this may be a possible translation. However, medieval and Renaissance sources such as Serranus of Nuremberg, 1539 [33], more commonly use "rupe" to mean a kind of tuber.

Eyne ander gute herte / Nym der wuerme engerlinge czweiteil / und regen worme das dritteteil / und czu stos sy und druck das saff durch eyn tuch / dorczu tu auch saff von steyn krawtes worczel / und stos doryn eyn gluende eizen ader was du herten wilt

Another good hardening method: Take two parts [rain-]worm larvae [or grubs] and three parts rainworm and mash them together. Press the juice through a cloth, and then add the juice of the Steinkraut root. And plunge the glowing iron in this, or whatever else you wish to harden.

The Latin botanical name for Steinkraut is *Lobularia Maritima*, or Sweet Alyssum in English. *Regenwurm* appears to be the same as English "earthworm", the kind of worm that comes out after it rains.

A formula for tempering blades:

Wiltu dy herte von dem eizen entloezen So nym menschen blut / Und los das sten bis das wasser dorof stet und wert / zo seige denne das wasser in eyn glas / und halt das / Und wen du denne dy herte entloesen wilt / zo nym das geherte wofen und halt das czu dem fewer bis das is zo heis werde das is das wasser slinde / zo stich daz wasser mit eyner veder an dy sneide zo entlet sich dy herte und wirt linder /

If you wish to temper the hardness away from iron, then take human blood, and let that stand until the water stands on top of it, and stays separated. Then drain off the water into a glass, and set that aside. And when you wish to take the hardness away, then take the hardened weapon and hold it in the fire until *it becomes so hot that water sizzles [presumably, when a drop of water is placed on the blade]. And then paint the water [from the blood] onto the blade with a feather; this will take away the hardness and make it tempered.*

The "water" is the serum from the blood, which separates from the more solid parts when the blood is left to stand.

Formula for annealing iron:

wiltu eisen weich machen und czehe / zo nym canomillen blumen eynteil / und eyn teil kranches snabel das hat bloe blun und eynteil veitbomes / Und das lege alles mit eynander / in heis wasser / und tu is in eynen tap / und decke is / das der broden icht aus moege gen und laz is wol siden Dorynne lesche gluende eisen / das wirt gar weich und czehe /

If you wish to make iron soft and tough, then take one part Camomille flowers, and one part Veitpommes, and one part stork's beak of the kind that has blue markings. And put that all together in hot water, put it in a pot, and cover it, so that the broth cannot escape. And let it simmer for a long time. Then quench glowing iron in it; this will make it soft and tough. [Note: Veitpommes is a kind of fruit or berry.]

Another formula for annealing iron:

wiltu eizen weich machen / zo nym horn und schabe das of eyn leder und menge das mit sal armoniaco / und seiche dorof / und winde das uem das eisen und laz das leder alzo of dem eisen vorbruen zo wirt is weich /

If you wish to make iron soft, then take horn and scrape that on [or "rub it into"] a piece of leather and mix that with Sal Armoniac. And then urinate on it, and wrap that around the iron. And then leave the leather to steep around the iron; this will make it soft. [Note: Sal Armoniac is Ammonium Chloride.]

Only late in medieval times, did sufficient technical advances in steel-making occur in Europe. In was only in the late 18th century that difference between iron and steel was identified as being associated with different quantities of carbon present [34][35].

It was not until 1890 that Adolf Martens made the discovery of the hardenable phase in steel, that we now call Martensite. It is remarkable that the ancient metallurgists, and blacksmiths were able to achieve the results they did, using only empirical methods.

Conclusions and Summary

From the earliest times, at the beginning of the Iron Age, quenching has played an important role in the growth of civilization throughout the World. Much of the development of quenching was developed out of mysticism, and empirical experimentation. It was not until much later, at the beginning of the Industrial Age (1850 AD or so), that mankind started on a quest to understand and quantify the mechanism of quenching and heat treatment. While much of the empirical technology developed was used to increase the effectiveness of swords, knives and armor, there has been a technology transfer to other devices important to the arriving Industrial Age. Today, there is a firm grasp on heat treatment, and the mechanism of quenching, enabling special quenchants to be tailored to specific application. It was these original philosophers, alchemists and blacksmiths that are the foundation of the Science and Art of Metallurgy today.

Figure 7. Museum quality armor created using modern quenchants. Photograph courtesy of Robert MacPherson, Armoror (http://www.lightlink.com/armory/armory.html).

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