# Environment versus sustainable energy: The case of lead halide perovskite-based solar cells

Supplementary material

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# *Environment vs. sustainable energy? The case of lead halide perovskite-based solar cells.*

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## Appendix

The purpose of this appendix is to provide the reader more background information on the historical exploitation of Lead, complementary to the manuscript. The most prominent applications are briefly outlined.

**Box A: The Ancient Near East (3500 B.C. - 800 B.C.)**

The ancient Egyptians were well acquainted with the use of lead since pre-dynastic times.[1] Being heavy and relatively inert to corrosion, lead was found purposeful for the making of weights and sinkers. Additionally, being malleable, it is was also used for the manufacturing of cheap statuettes and jewellery. Lead and its compounds were moreover recognised for their anti-septic properties and were among the first drugs of mineral origin to be used. The pharmacopoeia of Ancient Egypt preserved in the Eber papyrus and Hearst Medical papyrus dated at around 1550 B.C. feature a plethora of recipes in which many lead compounds (red lead, $Pb_3O_4$) and Galena (lead Sulfide, PbS) are used as astringents, external cooling agents and Collyria (eye salves).[2] There is evidence that Galena, the principal ore of lead, was widely used in the age-old eye-cosmetic *Kohl*.[3] As infectious conjunctivitis was common in ancient Egypt, *Kohl* was applied around the eyes to repel flies and other potential microbial sources of disease, concurrently reducing the glare of the desert sun. Similar applications for Galena are also recorded in the Old Testament and in the inscriptions of ancient Mesopotamian cultures. Particularly lead oxides are an integral part of the *materia medica* of the most primitive cultures. Ancient Babylonian tablets dated at 668-626 B.C. authenticate such use of lead compounds in plasters for therapeutic purposes.[4] Aside from medicinal use, several references are made to extractive metallurgy in the Old Testament entailing a profound awareness of lead processing and lead's desirable and versatile material properties.

*"As they gather Silver, and brass, and Iron, and lead, and tin, into the midst of the furnace, to blow the fire upon it, to melt it..."*(Ezekiel, 22:19-20)

*"Thou didst blow with thy wind, the sea covered them: they sank as lead in mighty waters"* (Exodus, 15,10)

**BOX B: Antiquity (800 B.C. – 500 A.D.)**

The Romans conducted the first mass production of lead after cupellation (refining process) was invented.[5] Lead, rarely found in its native metallic form is abundant in combination with Sulphur. The main lead-bearing ore is Galena ($PbS$), but other naturally occurring minerals are Boulangerite ($Pb_5Sb_4S_{11}$), Anglesite ($PbSO_4$) and Cerussite ($PbCO_3$). Being widely distributed in the Earth's crust, Galena is also an important Silver-bearing source.[6] In fact, the Romans mined Galena with the initial purpose to refine Silver, but found the ability to extract lead, up to then considered a waste product, by a rudimentary smelting process enabled by lead's relatively low melting temperature (327°C).[7] Realising its abundance and versatile properties, lead soon became the material of choice in numerous and diverse applications. Being soft, ductile and malleable, lead was easily exploited for the making of kitchen utensils, pots, urns, coins and kettles. Due to its longevity (i.e. corrosion resistance) and softness, it also became the preferred choice as roofing material. Furthermore, providing exceptional sealing, lead was most benefitted from in the Roman plumbing system consisting of lead pipes named *aqueducts*, allowing optimal transportation of water across the entire empire.[8] Most water brought to Rome by its aqueducts was used to supply its public baths, latrines, fountains and private households. To a lesser extent, they also provided water for mining operations, milling, farms and gardens. Notably, the etymological origin of the word *plumbing* and the chemical symbol for lead *Pb*, trace back to this ancient use and are derived from the Latin word for lead, *Plumbum*. By analogy, *Plumbism* became a synonym for lead poisoning.

Having few sweeteners besides honey, the Romans also used lead to produce sweetening agents. Roman vintners insisted on using lead pots or lead-lined copper kettles for winemaking. *"For boiling,"* wrote Roman vintner Columella, *"brazen vessels throw off copper rust which result in a disagreeable flavour"*.[9, 10] On the contrary, by boiling unfermented must in lead kettles for long hours, lead could seep out of the container, inadvertently artificially sweetening the wine. Continuing the boiling process to two-third, half or one-third of the original must volume, the sweet aromatic juices *carenum*, *defrutum* and *sapa*, respectively, could be obtained.[11] They were mainly produced to provide wine of bouquet and colour, but also served other culinary purposes such as sweetening and preservation. It is now known that the sweet taste of Roman wine is due to acetic acid ($CH_3COOH$) hydrolysing to form lead acetate ($Pb(CH_3COO)_2$) with lead ions seeped out of the hot container walls. Remarkably, in time, the Romans learned how to make the crystalline form of lead acetate by exposing litharge (lead oxide ($PbO$)) to vinegar—later named *Saturn's sugar*.[9]

Notably, aristocratic Roman women used *defrutum* for cosmetic purposes along with white lead ($2PbCO_3{\cdot}Pb(OH)_2$), later known as Venetian ceruse, that was commonly applied as an efficient face whitener.[4] The therapeutic applications of lead persisted into the Roman Period and became extremely widespread. As it was presumed that lead contained cooling properties, respected physician Soranus of Ephesus would recommend applying a piece of lead to the navel of a new-born child to help the wound cicatrise and meld properly into the cavity.[12]

**Box C: Middle Ages (500 – 1500)**

In the medieval period, lead was largely recycled from abandoned Roman cites, mainly anew finding purpose in roofing and plumbing. At the start of the 13the century, lead was frequently utilised in the emerging applications of coloured glass.[13] Though its use was widely known—as authenticated by a lead glaze recipe found on a Babylonian tablet dated at 1700 B.C. along with coloured Egyptian, Roman (e.g. Lycurgus Cup and the Portland vase) and Han-Period (China, 206 B.C.-220 A.C.) glass objects—it was not until the Medieval Period that the use of coloured glass culminated when it became a significant art form illustrating the narratives of the Bible to a largely illiterate populace.[14-16] Notably, lead was considered an imperative ingredient for the extensive production of glass. As the high temperature required for the melting of silica (>1500°C) was not attainable by all glass factories at the time, lead Oxide (PbO) was added to lower its melting temperature to <800°C.[16-18] According to a manuscript preserved in *Bibliotheca Marciana*, in such processes metallic lead was actively calcined to lead Oxide (PbO), which was used as an additive up to 40 wt% for the making of *lead glass*.[16] Furthermore, providing glass with lower viscosity and thereby rendering it much more fluid than ordinary soda-lime glass above softening temperature, lead glass paved the way for the vitreous enamelling of other glass, metal and ceramic objects. Also referred to as glazing, colour was imparted to the enamel by the addition of metallic salts (mainly oxides) during the glass manufacturing. Upon the addition of lead compounds, glass of yellow colour (also referred to as *incorruptible Gold*) could be obtained.[19] The resultant stained glass was either used as such, or was pulverised and processed into a moist paste for the painting of colourful details on other vitrified surfaces.[20] Today, a remarkable amount of ancient and medieval works of coloured glass can still be admired, among them impressive stained glass windows in churches, mosques and other significant buildings. Remarkably, glazing was also applied on diverse cooking ware, such as elaborate plates and goblets, intended for use by the privileged of the medieval period.[21] Additionally, the picturesque designs in the windows that are an assembly of smaller pieces joint together by a soldered network of lead, more commonly referred to as lead cames, represent an additional employment of lead in the Middle Ages. Their use was sustained into the modern period, thereupon spreading to decorative windows in domestic architecture called leadlight.[22]

In 1440, the development of the printing press spawned an entirely new application of lead.

Striving towards the production of high-quality printed books, lead became a key material for the production of durable types.[23] Remaining the main constituent of the type, lead was alloyed into a durable and hard metal that could take clear impressions from a mould without shrinking and thereby representing a fundamental solution to the problem of printing with movable types.[24] In the same period, lead was still increasingly used for the adulteration of wine. [25]

The most striking use of lead in the medieval period can be ascribed to the firearm discovered in the 13th century China. Despite lead being more expensive than Iron, it became the chief material for the making of bullets.[26] As it was abundant and easy to process using an ordinary wood fire (owing to lead's low melting temperature) and realised better velocity retention (because of the high specific density), lead shot was greatly favoured. Moreover, being soft, lead shot imparted less damage to the iron gun barrels upon firing.

**Box D: Early Modern Period (1500 – 1789)**

Entering the modern era, lead once more revolutionized the glass industry. Though its use as an additive was already common, it heralded the production of English *lead Crystals*, patented by George Ravenscroft in 1673.[27] lead, besides making glass more fluid at much lower working temperature, also induces a higher density of the glass, resulting in a higher refractive index and more attractive optical properties, and thus enabled the manufacturing of perfectly clear and flawless glassware on an industrial scale. Thereafter, as a measure of quality, glass was sold by weight and by its characteristic ringing sound when tapped on.

Another reoccurring application of lead was the 16th century cosmetic Venetian ceruse. Remaining in practice since Roman times, white lead, symbolising European aristocratic modesty, had become the cause of death of famous society hostess Maria Coventry in 1760.[28] Also the pale complexion of Queen Elisabeth I was attributed to this so-called "mask of youth". Later named the *Spirits of Saturn*, the use of Venetian ceruse lasted until the late 18th century in Europe, reappearing in the same period in Japanese culture as a cosmetic for traditional hostesses known as *geishas*. [29]

**Box E: Late Modern Period (1789 – 1945)**

A major demand for lead in the late modern period came from the plumbing and painting industry. White lead, which was already being produced on a smaller scale during the 4th century B.C. (as described by Vitrivius and Pliny the Elder), was favoured for its opacity and density allowing the coverage of large surfaces with minute quantities.[30-32] Moreover, upon the addition of lead(II) chromate ($PbCrO_4$) and lead (II,V) Oxide ($Pb_3O_4$), the pigments *chrome yellow* and *lead red,* respectively, could be obtained. Lead, providing paint with increased durability (corrosion resistance) and faster drying, paved the way for the widespread use of such paints in domestic and industrial applications until 1978.[33] To date, leaded paint is still used to a small extent, such as in marine applications.

During the early 20th century the hazards from ionizing radiation were recognized and the use of lead and other materials became commonplace for shielding against X-rays. By the 1920's appropriate shielding materials were identified and more knowledge on interaction of matter and radiation was acquired. Due to its high mass density arising from its high atomic number, lead was discovered to effectively absorb the energy of gamma and X-rays. With the development of high-energy medical accelerators after 1940, new and more complex shielding problems were addressed and the development of lead shielding became a major necessity.[34, 35] In addition to bringing major value to the medical field and public health, it also enabled deeper understandings in nuclear research and provided the essential protection in institutions and government bodies involved in scientific experiments.

By World War I, lead-Copper core-shell ("jacketed") bullets were used to prevent lead deposition inside the gun and preserve bullet aerodynamics.[36] The jacketed bullet was further modernised and various types have been used in World War II. Today, jacketed lead bullets remain common and are commercially available for use in handguns and rifles. It is estimated that from Pearl Harbor to V-J Day, the Industry- Ordnance team furnished to the army and 43 foreign nations 47 billion rounds of small arms ammunition and approximately 11 million tons of artillery ammunition.[37]

**Box F: Contemporary History (1945 – 2017)**

By the end of the World War II, the main application of lead was the lead-acid battery.[38, 39] With their ability to supply high surge currents and quick charging rate, they were initially used by The Hudson Motor Car Company to supply energy to electrical starters of early motor vehicles. Today they remain the technology of choice for automotive SLI (starting, lighting and ignition) applications, with about 3 million tons of lead used for their manufacturing in 1992 and an estimated 320 million lead-acid battery units shipped in 1999.[40] Another automotive-related utilisation of lead was its use as an anti-knocking agent. As evidenced in the aircraft engineering from 1916-1919, engine knocking was a frequently occurring failure in high performance engines that require higher compression ratios.[41, 42] The combustion of the air-fuel mixture that is set to start as a precise response to the ignition by the spark plug would rather explode outside the envelope of the combustion front in multiple pockets of air-fuel mixtures. Resulting in a shockwave with a characteristic metallic 'pining' sound, catastrophic failures, such as a complete rupture of the combustion chamber, could be generated. With the introduction of lead additives as anti-knocking agents to gasoline by 1920, the fuel could withstand much more compression (higher octane rating) before its ignition, thereby allowing the use of much more powerful higher compression engines.[43] The latter played an important role in World War II, as it enabled the use of supercharged engines. Today, the octane booster—tetraetyllead—is still used as an additive in some grades of aviation gasoline, and in some developing countries. Remarkably, an additional advantage of lead based anti-knocking agents were their quality to prevent exhaust valve and valve seat wear.

Furthermore, since the 1930s-1940s, lead in the form of lead hydrogen arsenate ($PbHAsO_4$) was prepared by farmers at home as a pesticide primarily against the potato beetle. In the U.S. it was first used against the gypsy moth in Massachusetts as an alternative to the highly toxic Paris

Green pesticide.[44, 45] Owing to better adherence to the surface of plants and thus enhancing its prolonged insecticidal effect, lead hydrogen arsenate was of preferred choice until 1919 when a search for a substitute commenced. Other uses of lead hydrogen arsenate include the battle against the codling moth, considered an agricultural pest in the fruit industry. It remained being used until it was officially banned as an insecticide in 1988.

Perhaps the most prolific use of lead in contemporary history besides lead-acid batteries is that in solder.[46] Evidence suggests that soldering was employed as early as 5000 years ago in Mesopotamia. Originating in the early history of metalworking, it was most often used for the making of jewellery, cooking ware, tools and other uses such as assembling stained glass. Providing a reasonably permanent but reversible connection, it started to be more commonly applied in plumbing as well as jointing sheet metal objects such as food cans, roof flashing and rain gutters. Today, soldering is mostly seen in connections of electrical wiring and electrical components in printed circuit boards. The most common and preferred metal alloy for soldering are the Sn-Pb mixtures. Though historically higher portions of lead (50/50) were used to allow the alloy to solidify more slowly, the 60/40 Sn-Pb and the eutectic 63/37 Sn-Pb remain the most favoured solders. Extensive studies have demonstrated that the latter provide a wide processing window that is generally difficult to cover with current lead-free, high tin content solders.[47] In plumbing, lead solder remained in use until the 1980s, providing desirable water tightness. With the implementations of the RoHS and WEEE directives, lead-free solder with high tin content is more expensive and brittle with questionably improved wetting properties. Overall it can be stated that the latter solders are considered technically inferior in terms of electrical properties and long-term stability. In addition, virtually all electronic assemblies were designed to withstand at best the temperatures required for the application of lead-tin solder, so the risk of failure increases dramatically upon the application of lead-free solder instead (that requires higher temperatures). Furthermore, the exhaustive reliability and easily inspectable characteristic appearance of lead-tin solders are now only within reach for exemptions of the RoHS directive.[48] Anno 2017, the persistent utilisation of lead can be categorised as follows: batteries (80%), rolled extrusions (6%), pigment (5%), ammunition (3%), miscellaneous (3%), alloys (2%) and cable sheathing (1%).[39]

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