MOLYREVIEW

INTERNATIONAL MOLYBDENUM ASSOCIATION

January 2011

Heating homes with household waste

Photo: JM Treuil / SYCTOM

Located only minutes from the Eiffel Tower, a new waste-to-energy plant recently started operation in Paris. The plant uses the waste of more than one million households to produce heat and power for many homes here. It operates in a way that saves energy and is friendly to the environment and its neighbors. Molybdenum-containing materials are used throughout the plant to ensure the reliability of processes at high temperatures and in highly corrosive environments.

Just outside Paris, on the banks of the Seine, a new waste-to-heat and power generation facility recently began operation. The facility collects the household waste of some one million inhabitants in the Paris metropolitan area and transforms it into heating for homes and electricity. No white steam plume or chimney stack betrays its presence. Tourists on pleasure boats that cruise the city's historic waterway would never guess that the elegant wood and metal facade houses a sorting and incineration plant 31 meters below ground. In this regard the plant is a miracle of form and function, blending unnoticed into one of the world's most beautiful cities.

The plant, known as "Isséane", was designed to be an exemplary model of integration into the urban environment. By any environmental quality criteria it is truly "green".

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Molybdenum and our health

If there is anything we can all agree on, it is that we want to live a healthy life. We know the basic things we can control to help achieve this, such as plenty of exercise, rest and good food. When it comes to healthy eating, molybdenum participates in a number of chemical processes within our bodies that are important for good overall health. Fortunately, it is easy for us to obtain our daily molybdenum requirement by eating commonplace nutritious foods such as dark leafy vegetables and legumes.

High on the list of things that are important to us is our health. Even when we feel well we continue to pay heed to advice about living a healthy lifestyle. We want a lifestyle that includes adequate sleep and exercise. We also want to make sure we eat good foods to ensure our bodies receive proper nutrition and essential vitamins and minerals.

We usually think of molybdenum as a metal which occurs in a mineral encountered in mining – the mineral "molybdenite" – as the source of molybdenum compounds and molybdenum metal. But do you know that molybdenum is essential to the proper functioning of one's body? Our bodies require some molybdenum intake each day. Fortunately this is accomplished effortlessly through the food we eat and the water we drink! It's important, however, to know about the role molybdenum plays, and about those circumstances that contribute to maintaining a molybdenum-healthy body.

What does molybdenum do in our bodies?
Molybdenum occurs and participates in the function of three important enzymes within our body. Enzymes are chemicals that act as catalysts to facilitate important biochemical reactions, sending the reaction in the desired direction and speeding it up. Without enzymes, many essential chemical reactions would not proceed rapidly enough to support life.

Molybdenum is a component of three enzymes: xanthine oxidase, sulfite oxidase and aldehyde oxidase.

Xanthine oxidase has an essential role in the breakdown of waste nitrogen compounds and their elimination as uric acid in urine. It also helps the body to utilize its iron reserves and assist with the burning of excess fat.

Sulfite oxidase is required to metabolize the sulfur-containing amino acids cysteine and methionine in foods. It oxidises toxic sulfites taken in with food to sulfate.This is the last step in the metabolism of sulfur-containing compounds, after which the sulfate is excreted.

Aldehyde oxidase assists with oxidation to produce non-alcohol compounds in the liver. It therefore helps to avoid alcohol-induced liver injury. Aldehyde oxidase also works to detoxify a wide variety of organic compounds, toxins, nitrogen wastes and other pollutants entering the liver.

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Content

Moly Review

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Moly is necessary to keep us healthy. Photo: istockphoto.com/skynesher

Recommended Dietary Allowances (RDAs) for individual elements according to the Food and Nutrition Board, Institute of Medicine, U.S. National Academy of Sciences 2001

Life stage	Age (yrs)	Mo (µg/d)	Ca (mg/d)	Fe (mg/d)
Infants	0–12 mo	2–3	210–270	0.27–11
Children	1–3 4–8 9–13	17 22 34	500 800 1,300	7 10 8
Adolescents	14–18	43	1,300	11–15
Adults	19+	45	1,000–1,200	8–18
Pregnant Women	All	50	1,000–1,300	27
Breast Feeding	All	50	1,000–1,300	9–10

Source: Food and Nutrition Board, Institute of Medicine, U.S. National Academy of Sciences, 2001

What effects occur in our bodies?

When our body contains sufficient molybdenum and is functioning at a molybdenum-healthy level, a number of beneficial effects have been claimed regarding:

- alertness and concentration
- metabolism of fats and carbohydrates
- dental health and reduced tooth decay
- some protection against stomach and esophageal cancer
- reduced sulfite-reactive asthma attacks
- some protection against anemia
- general maintenance of proper cellular function and body growth

Since most people receive sufficient molybdenum in their diet, adverse health effects due to insufficient molybdenum are rare. If a molybdenum deficiency does exist, it could appear as the opposite of the beneficial effects noted above.

A well-known example attributed to an insufficiency of molybdenum in the diet occurred in Linxian in northern China. The soil there is low in molybdenum and thus the dietary intake from plants is also low. Here the occurrence of cancer of the stomach and esophagus is high, a direct or indirect consequence that is attributed to the low molybdenum.

Our need for molybdenum and its source

Health authorities seek to establish recommended daily intakes for minerals essential for human health. Molybdenum is included on the list. The amount required depends on a number of factors such as age, sex, pregnancy and other variables. The accompanying table shows a comparison between daily molybdenum requirements and those of two other minerals considered important. The amount of molybdenum needed is much less than that of calcium and most other minerals.

Molybdenum readily passes through the body, so we need to take it regularly. Our primary source of molybdenum is food, although some may also be found in drinking water. Fortunately, foods nearly everywhere can supply our needs, especially dark leafy greens and legumes. These foods absorb molybdenum from the soil and pass it on to us when we consume them. The most important consideration is to maintain a healthy and varied diet. Following is a list of foods that are good sources of molybdenum. Molybdenum is also available in over-the-counter dietary supplements.

Good sources of molybdenum

- legumes (beans)
- cucumbers
- collard greens and spinach
- whole grains
- peas
- nuts
- sunflower seeds
- meats, liver

We are indeed fortunate that our favorite metal does so many good things within our bodies and is so easily accessible. Healthy dinner anyone? (ck)

A balanced diet supplies all the molybdenum needed. Photo: istockphoto.com/kcline

Can molybdenum help provide the ideal energy source of the future?

Hydrogen is the ideal fuel for the world's future clean energy needs. Unlike oil, gas and coal that produce the greenhouse gas CO_2, the acid rain pollutant SO_2, and other toxic compounds, hydrogen produces only non-polluting water as a combustion product when it is burned. Hydrogen can be used to power cars and fuel electric power plants and fulfill many other energy needs. Additionally, the "hydrogen cycle" would not require the heavy investment in anti-pollution equipment needed by fossil fuels. Thus researchers have been working for many years to find a practical way to make this energy source readily available. The recent discovery of a molybdenum compound that catalyses the formation of hydrogen by electrolysis of water has attracted much interest in light of this quest[1]. This new compound, an efficient and robust catalyst, has been billed as taking us "a step closer" to obtaining cheap hydrogen fuel from seawater[2].

Most of today's energy needs are supplied by fossil fuels in the form of oil, gas and coal. The ever-growing world demand for energy, the environmental impact of fossil fuels, and their limited supply, have forced us to develop alternative energy sources. However, all of them come with their own set of problems and drawbacks. Solar energy can only be generated during daylight and must be stored for use at other times. Similarly, wind energy can only be generated when wind is blowing sufficiently, and has to be stored to even out fluctuations in production.

Hydrogen stored in tanks for industrial use. Photo: istockphoto.com/bentrussell

Hydrogen has the potential to solve many of the problems related to other energy sources. It has a high energy content per gram, its supply (from water) is essentially unlimited, it is transportable, and it is completely non-polluting when burned. Were hydrogen readily available it could be used in fuel cells to power cars, in power plants to make electricity, and in many other applications.

Unfortunately, hydrogen is not readily available to us in its most usable form, the hydrogen molecule H_2. It exists naturally only in other molecules, for example in natural gas (methane – CH_4) and water (H_2O). Current technologies to produce hydrogen from these sources are far from ideal with respect to cost and capacity.

Our supply of hydrogen today

Today we produce most hydrogen (95%) from methane through steam reforming, a process based on the reaction of water with methane:

$$CH_4 + 2H_2O \rightarrow CO_2 + 4H_2$$

This process gives us the highest, cleanest energy form of hydrogen, the H_2 molecule. However, it uses methane and coal as feedstocks, and requires considerable energy input, since the process takes place at 900°C. This technology suffers from limited fossil fuel supplies and is associated with major negative environmental impact due to the carbon dioxide produced by the reforming reaction and its implication in global warming.

The one hydrogen source available to us with essentially unlimited supply, and potentially no environmental impact, is water. A dream of chemists for many years, or the chemists' "holy grail", has been to find a cost-effective way to split hydrogen from the oxygen contained within the water molecule:

$$2H_2O \rightarrow 2H_2 + O_2$$

Processes have been developed for doing this, and are based on using sunlight or cleanly generated electricity to promote the water-splitting reaction on a surface such as an electrode. These processes work, but they are slow and inefficient, and cannot produce hydrogen at acceptable costs. What has been needed is an effective way to speed up the process, a suitable catalyst. Catalysts are compounds that speed up a chemical process without being permanently changed by it. Molybdenum compounds are used as catalysts for several other important chemical processes. Now chemists and the energy world are excited about a new molybdenum-containing catalyst that could speed up the hydrogen generating process. →

1 Hemamala I. Karunadasa, Christopher J. Chang, Jeffrey R. Long, Nature, 2010, 464, 1329. A molecular molybdenum-oxo catalyst for generating hydrogen from water. [University of California, Berkeley.]
2 Lin Edwards: http://www.physorg.com/news191745752.html.

Hydrogen auto fuel is now available at some service stations. Photo: istockphoto.com/f00sion

The exciting new discovery

Chemists already knew that certain compounds containing molybdenum or other elements catalyze the water-splitting reaction. However, these compounds were used up during the reaction and the reaction speeds were too slow. A new compound was needed that could be recycled while functioning to produce large volumes of hydrogen – a stable catalyst. ***Just such a new compound has been discovered!*** The compound is created, on a molecular scale, by encapsulating the molybdenum atom in the form of the Mo^{4+} ion within an organic molecule that uses a nitrogen atom to bind the molybdenum. (An ion is an atom that has gained or lost one or more electrons.) The geometric construction of this molecule showing how component atoms are arranged around the molybdenum ion is shown in the figure below.

X-ray structure of the catalyst cation $[(PY5Me_2)MoO]^{2+}$: Mo, green; O, red; N, blue; C, gray. H atoms not shown. Image credit Ref. 1 (Nature, doi:10.1038/nature08969).

The beauty of this molecule is that its salts are soluble in water and that the molybdenum will operate in two oxidation states*, Mo (II) and Mo (IV). Molybdenum's ability to undergo changes of oxidation state with changes in the number of electrons associated with the molybdenum (its "double personality") makes the process potentially very practical. This is because electric current can be passed through water to control molybdenum's oxidation state while electrons are donated to produce H_2 from the water. What is happening here is something almost like a perpetual motion machine that works with the help of a small amount of electricity.

While the improvement in reaction speed over traditional processes is not as high as some alternative approaches, this concept has a major advantage: its robustness. The Mo^{2+} ion is trapped in the organic molecule, so is not lost in the solution but is used repeatedly. Another very attractive property of the catalyst is that it is not sensitive to the many ions present in seawater. It is equally effective in both fresh water and seawater without extensive pre-treatments – ***it is thus capable of providing an endless supply of hydrogen***.

Where to go from here

Is this a real breakthrough likely to make its way into practical applications? As with many new developments and discoveries, there will be many hurdles to overcome before a commercial process evolves. For example, this particular catalyst's need for a complicated organic molecule could be a stumbling block. We should perhaps think that we are now at a "proof of concept" stage. The challenge is to incorporate molybdenum on, for example, the surface of an electrode in its new highly effective catalyst form.

One always likes to look ahead when new developments are on the horizon, and this discovery is truly "really new". An abundant supply of hydrogen could solve the global warming crisis as we transition away from our present hydrocarbon-based energy system. (pm)

Notes:
** The oxidation state denotes the number of negatively charged electrons an atom has lost or gained when it becomes an ion. Thus Mo^{2+} has lost 2 electrons and Mo^{4+} has lost four electrons, compared to the uncharged molybdenum atom*

Hydrogen fuel cells produce useful energy just as batteries do. Photo: istockphoto.com/gchutka

Continued from page 1

Heating homes with household waste

The basic process

Waste materials entering the plant have already been sorted by community households into glass, plastic and metals, paper and non-recyclables in accordance with EU waste treatment regulations. A number of further steps are employed to complete the separation of recyclables, including mechanical sorting, magnetic separation, and visual sorting by operators and optical systems. With a recycling capacity of 22,000 tons per year, many loads of recyclables are returned from the plant each day to different industries for conversion to useful products.

The remaining non-recyclable waste stream accounts for 460,000 tons of combustible materials each year. This waste is converted into energy using a reliable and proven incineration process where temperatures reach 1,000°C. The waste becomes the fuel in a furnace in which hot combustion gasses and solid residue, called clinker, are produced. During the process all organic materials, pathogens and microbes are destroyed by the high combustion temperatures. The clinker is usefully recycled for surfacing roads, and the hot combustion gases become the starting point for energy production.

Conversion of heat to steam

The heart of the energy conversion process is a chamber similar to a boiler in a conventional fossil fuel power plant. Water at a pressure of 50 bar is passed through the chamber in a system of pipes. The hot combustion gas in the chamber heats the water in the pipes to 400°C. The pipes must withstand the effects of high pressure and temperature, and the corrosive effects of the gas. The pipes are, therefore, made of Alloy 625 (N06625, EN 2.4856), a nickel base alloy containing 25% chromium and 9% molybdenum. The unique combination of Ni, Cr and Mo gives it very good strength and excellent resistance both to stress corrosion during operation and to acid condensate corrosion that can occur during down periods.

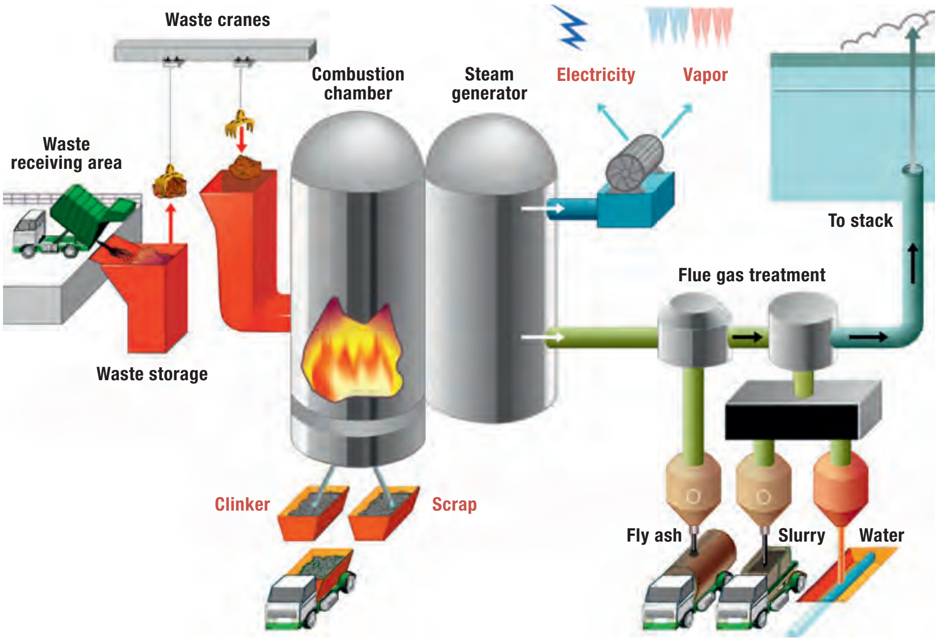
The energy contained within the high-temperature, high-pressure water is then converted into steam in a steam generator downstream from the chamber. The plant contains a dual furnace – dual steam generator system, having the capacity to produce 200 tons of steam per hour.

Steam utilized for electricity and heat

Steam exiting the steam generator at 400°C and 50 bar drives a steam turbine which in turn drives an electric generator. Molybdenum plays an important role in the turbine. Many parts are manufactured from molybdenum-containing alloys such as Alloy 625 and Type 316 stainless steel (S31600, EN 1.4401). Some important parts are the steam nozzles that direct the steam onto the turbine blades causing them to rotate. The good corrosion and wear properties of Type 316 stainless steel make it ideal for this application.

The steam turbine drives a 52 MW electric generator, providing sufficient electrical power for the facility's needs, and an excess which is sold to the national grid.

Exhaust steam at lower pressure and temperature is a valuable by-product, which is delivered to a local network supplying the heating requirement of 79,000 homes. ➔



Flow diagram of the plant showing how energy (waste) enters and leaves as useful electricity and heat, useful byproducts and clean flue gas. Credit: SYCTOM

Odorless and invisible releases

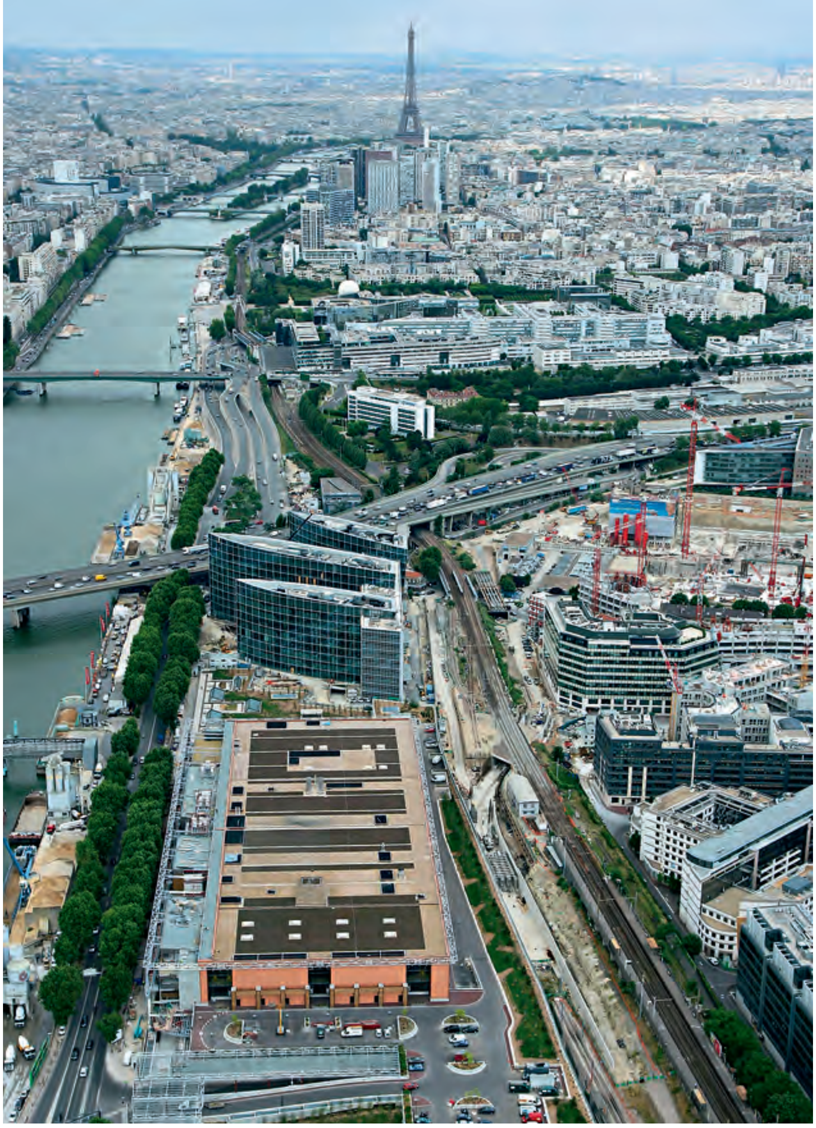
A very important final step of the process is the purification of the combustion gas before it exits the plant. This step decisively contributes to the high environmental quality of the Isséane plant. Purification of the flue gas begins with a scrubber which removes dust, acid gases and heavy metals by absorption in a neutralizing liquid media. Subsequently, the flue gas passes through a de-nitrification facility for the removal of nitrogen oxides (NO_x).

Nitrogen oxides are air pollutants that must be reduced to a minimum to limit their health impact. The de-nitrification facility employs the catalytic reduction of NO_x in contact with ammonia (NH_3). The end products are water and nitrogen, both normal and essential components of the air we breathe. Here again molybdenum plays an important role. The entire ammonia-water system is constructed of Type 316L (UNS S31603, EN 1.4404) stainless steel piping, chosen for its high resistance to acid corrosion. Using this process the NO_x emissions are reduced well below the threshold imposed by European regulations.

A winner for energy, environment and neighbors

A complete material and energy balance of the plant yields a startlingly favorable outcome for the environment and the impact on the surroundings. The transformation of waste to energy by the plant avoids the consumption of 110,000 tons of new fossil fuels (coal, etc.), and the associated emission of 330,000 tons of carbon dioxide (CO_2) into the atmosphere each year.

Given that more than 50 percent of the energy present in the non-recyclable waste comes from renewable materials such as plants and trees (regenerative energy), more than half the energy produced is CO_2 neutral. This further helps reduce greenhouse gases responsible for global warming.

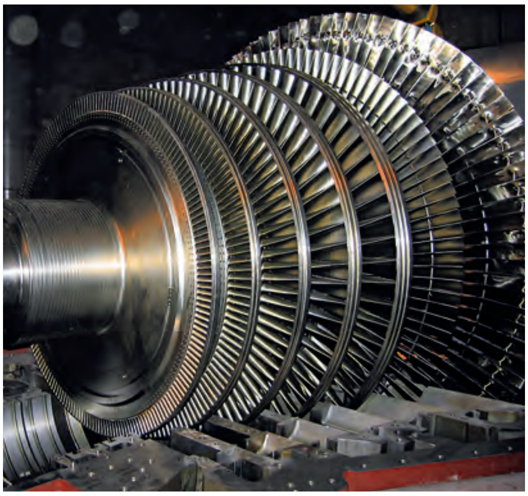


Aerial view of the waste plant. Photo: SYCTOM

Compared to other thermal processing facilities, Isséane produces lower emission levels because of its high efficiency and advanced combustion gas cleaning technologies.

The pictures of the plant in this article show that it does not intrude on the urban landscape but coexists in an aesthetically pleasing way with its neighbors. Indeed, Isséane has served many competing interests well, so that all have emerged as winners. (tp)

One of two steam turbines used to produce electricity. Photo: SYCTOM



View of the waste plant façade facing the Seine. Photo: SYCTOM

“There was never a good knife made of bad steel”

(Benjamin Franklin)

Kitchen knives require a demanding set of properties in order to do their job effectively. Molybdenum is an important ingredient in the highest quality cutlery steels, allowing them to perform with a hard, sharp, wear-resistant cutting edge.

Ask any professional chef what the most important kitchen tool is and the overwhelming response will be “the knife”. Of course, the professional chef doesn’t want just any knife, he or she wants *the knife* – words like “good” and “quality” are always used to describe their tool of choice.

The variety of kitchen cutlery available is overwhelming so an adjective such as “good” can mean many things. Some of the criteria for a good knife may be subjective, like the balance, the handle, and the shape. However, the heart of a knife is its blade and the steel from which it is made.

Most knives found in professional kitchens use chromium-containing steel for corrosion resistance. They use “high-carbon” steel because of carbon’s ability to produce high hardness and good wear resistance. But just as even a simple egg dish tastes remarkably different depending on the other ingredients, the high-carbon steel used to make knives can be created from a number of different recipes. Top cutlery makers, from Japan to Germany to America, offer high-carbon blades of varying compositions, each striving to meet the exacting needs of the chefs and cooks who use their products.

Aside from iron, chromium and carbon, many other ingredients contribute essential qualities to kitchen knife steel; however, all of the high-quality knives preferred by professional chefs include molybdenum in order to meet their high standards. To understand why steel made with molybdenum is so vital to creating the perfect kitchen knife, it is important to understand the requirements of a knife that will endure in the kitchen.

The kitchen knife is used from preparation to presentation – cutting, slicing, smashing and, even in the best kitchens, occasionally opening boxes or jars, and performing other tasks the knife is not necessarily designed for. For a chef to consider a knife “good” the blade must accomplish these tasks and in so doing meet the following criteria:

1. It must be strong enough to do all tasks without bending, distorting, buckling, warping, bowing, or breaking.
2. Its steel must be hard enough to create a very sharp edge. The harder the steel, the sharper the blade.
3. A knife blade must also maintain its sharp edge. Steel with hard carbide particles will remain sharp longer than one without carbides.
4. A knife cannot be so hard that it is brittle. Chips, abrasions, grooves and pockmarks reduce a knife’s cutting ability. Grease can become stuck in these defects and bacteria grow there, leading to unsanitary conditions. Durability and toughness are paramount to prevent defect formation and fracture.
5. The blade must be stain resistant, or rustproof. Rust creates some of the same unsanitary conditions noted above.

Molybdenum in these steels enables knives to have the above qualities – blades that are hard and durable while providing good edge retention and ease of sharpening, good stain and wear resistance and high strength without brittleness. Molybdenum strengthens the steel by its very presence as a basic alloying element in the material, the well-known alloy hardening effect. Moreover, molybdenum steels respond more effectively to heat treatment, the basic process used to make high-hardness steel. Finally, during heat treatment molybdenum combines with the carbon present in the material, creating hard carbides that improve the knife’s resistance to wear and keep the blade sharp for a longer time. Molybdenum also increases steel’s toughness, making the blade more resistant to chipping, pitting, and fracture. As if these advantages were not enough, molybdenum increases the steel’s resistance to corrosion, especially pitting corrosion caused by salty liquids and foods, which can lead to unsanitary trapping of food and resultant bacterial growth. It is no surprise then, that molybdenum-containing steels are a material of choice for professional cutlery.

“A good set of knives enables you to work quickly and efficiently. Keep them sharp – blunt knives are inclined to slip off food into waiting fingers.” (Gordon Ramsay) Photo: istockphoto.com/perkmeup

Of course, these high-performing knives are not only the result of a chef wanting a sharper blade. As one of humanity’s most ancient tools (knives date back →

"Knives are the best friends a cook can have." (James Beard) Photo: istockphoto.com/Alija

2 1/2 million years), humans have been tinkering with the knife in pursuit of creating the perfect tool for a long time.

Chefs, knife manufacturers, and materials suppliers working together have recently developed a notable new blade material. In 2003, realizing the demand for, and particular needs of kitchen-specific steel, one producer worked with top knife makers from around the world to develop a new steel grade specifically for kitchen knives: CPM® S30V[1]. This steel originated thirty years earlier in defense-related research on jet engine materials. Research lead to a process whereby very highly alloyed steels are atomized into metal powders in a high-tech version of a process like perfume atomization. The powders are then turned back into solid metal by pressing at high pressures and temperatures in a process called hot isostatic pressing (HIP). The process allows metallurgists to use much higher amounts of hard, wear-resistant additives like carbon and vanadium without incurring the brittleness that would occur in a conventional cast and forged steel. Hence, a blade was developed that is now considered by many to be one of the premium cutlery steels.

High-quality knives use many different steels. The following list identifies some of the more popular grades in a general order of decreasing wear resistance. The accompanying table lists typical chemical compositions, and the very high carbon, vanadium and molybdenum content for the CPM® S30V alloy shows why it has such outstanding properties.

SG-2: This steel is considered to be one of the top blade-making materials. Like CPM® S30V, it is made from powdered metal. The cutlery company Shun uses this steel for their Elite series of knives, which are some of the sharpest knives available.

1 A trademark of Crucible Materials Corporation

VG-10: This steel also produces very sharp blades. It is also very durable and has excellent edge retention. A variant of this steel is VG-1. It is very good but VG-1 does not produce as sharp a blade as VG-10.

Types 440/A/B/C steels: These are variations of the basic 440 stainless. The 440B and C variations contain higher carbon thus giving harder, more durable blades. This family of steels does not contain additives like vanadium that provide the highest hardness, so they are not at the top of the list in terms of wear resistance.

X50CrMo15 or similar steel variations: Wusthof and some other companies label their blades with this material designation. Less well-known brands often use this material for their knives, which can in many cases be purchased at very good prices. They make acceptable kitchen knives.

These steels all have two things in common: a very precise list of ingredients and tightly controlled processing. This combination enables them to do their job. Overlooking any ingredient or process step will produce an unacceptable blade. Key ingredients are chromium for corrosion resistance; carbon and vanadium for hardness, strength and wear resistance; and molybdenum working in its usual magical way to produce the best possible combination of properties. In all of these steels, molybdenum is a key ingredient. Without it, the chef's favorite tool would be incomplete. So, the next time you want to try a new recipe, make sure you have the right tools on hand, and – as importantly – make sure your knife is made from the right ingredients. (as)

The chemical composition of various cutlery steels (wt%)

Steel	Carbon	Chromium	Vanadium	Molybdenum
CPM® S30V	1.5	14	4	2
SG-2	1.4	17	2	2.2
VG-10	1	15	0.2	1
440C	1	17	0	0.4
X50CrMo15	0.5	15	0.2	0.7

"Keep your knives ever sharp and – toujours bon appetit!" (Julia Child) Photo: istockphoto.com/plastic_buddha

The unsolved riddle of molybdenum and corrosion

Though it is unknown to most people, the second law of thermodynamics controls all the natural phenomena that take place in our Universe. One of its consequences is that all metals except gold will corrode. Molybdenum changes neither the law nor its ultimate consequence regarding corrosion. Nonetheless, it greatly slows the corrosion process and makes for very practical, highly corrosion-resistant alloys, even though we are not sure why it has this effect.

Most of us are familiar with the many applications of stainless steel. Simply look around and you will find a wealth of uses for these non-corroding alloys, including industrial process equipment, architecture, and even tableware and cookware. These applications all have one thing in common: the stainless steel remains bright and shiny after many years of use. Stainless steels resist corrosion by forming a very thin protective (passive) film on the surface, which is produced by the chromium (Cr) and molybdenum (Mo) in these alloys. In contrast, ordinary steels are susceptible to the ever-present peril of rust. Exposure to air and moisture can cause a shiny ordinary steel object with very desirable properties to return to its oxide, and become a brown stained piece of debris. This problem has created a vast market for stainless steels which resist oxidation and corrosion in harsh environments.

Most metals we use every day begin their life cycle as oxides or other chemical compounds found in ores contained in the earth's crust. We mine the ore and refine it to produce a useful metal. Rusting (corrosion) that occurs during the metal's use is the natural process of the metal returning to its oxide form. Preventing this cycle from proceeding to completion, or preventing corrosion, is no easy task. One way to prevent corrosion on metals is through protective coatings. Plain carbon steel requires such rust-stopping coatings applied externally; aluminum requires a special anodizing process to impart corrosion resistance; copper alloys form a protective thick tarnish coating naturally. Stainless steels form their own coatings, passive films, by chemical reaction with the corrosion environment. This raises several questions: Why do metals want to return to their oxide form? How does corrosion produce a protective film on the surface of stainless steel? How does the protective film do its job? What is molybdenum's role in stainless steel?

The second law of thermodynamics

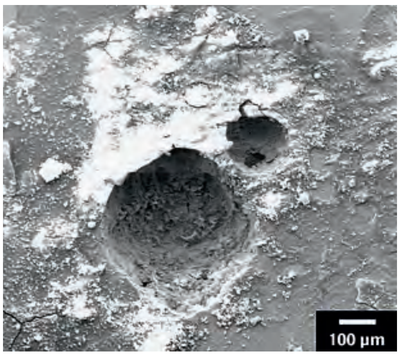
Corrosion is a result of the most basic law of nature, the second law of thermodynamics. Thermodynamics mavens have stated this law in many ways, for example:

- "Usable energy is irretrievably lost in the form of unusable energy."
- "Energy and matter in the Universe always becomes less useful."
- "All things want to reach their lowest possible state of free energy."
- "All metals except gold want to exist as an oxide or sulfide."

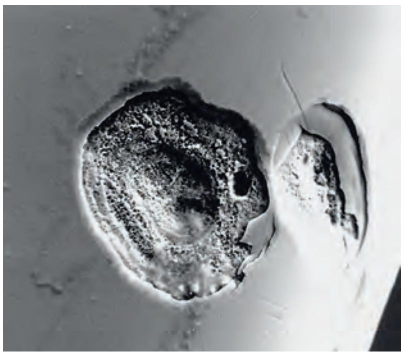
Free energy, the usable energy in a system, changes when something changes from a particular form to another. If the change occurs naturally, the free energy change will be negative because the final state has a lower energy than the starting state. A simple example is the case of a ball placed on the top of a hill – the slightest push will cause it to roll to the bottom of the hill, and the associated free energy change will be negative. Free energy quantifies the energy change for the process, and we usually state its magnitude in joules. For the cases of iron or chromium reacting with oxygen to form iron or chromium oxides at room temperature, we have the following chemical reactions:

$$3/2\,Fe + O_2 \rightarrow 3/4\,Fe_2O_3 \qquad \Delta G = -540KJ$$
$$4/3\,Cr + O_2 \rightarrow 2/3\,Cr_2O_3 \qquad \Delta G = -690KJ$$

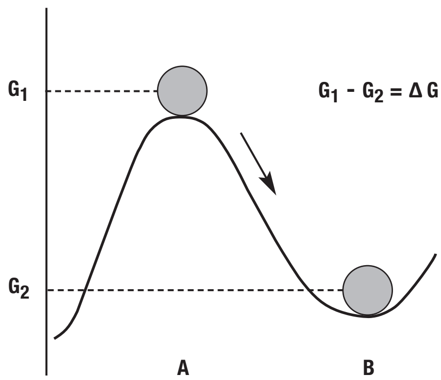
→



Deep pitting corrosion on Type 304 stainless exposed to salt. Photo: TMR



Electron microscope image of the inside of a small corrosion pit. Photo: TMR



The free energy change taking place when a ball rolls down a hill. G_2 is less than G_1 so the free energy change is negative.

The formation of chromium oxide has a greater negative free energy change than the formation of iron oxide (compare the two values), so it is the more stable compound. Chromium oxide thus forms instead of iron oxide. We call the chromium oxide layer a passive oxide layer because it is highly resistant to further reaction once formed.

Well then, why does chromium oxide protect against corrosion, while iron oxide does not? The answer lies in a basic difference between the iron oxide that forms on iron, and the chromium oxide that forms on stainless steel. In order for the oxide to protect against corrosion it must inhibit the movement of oxygen and metal atoms through the oxide layer. Iron oxide is relatively porous, and allows atoms to pass rapidly through the initial surface oxide and produce continued corrosion. On the other hand, chromium oxide is less porous so it restricts movement of atoms across the passive layer. In fact, the rate (kinetics) of oxygen, iron, and chromium movement through the passive oxide film is so slow that for all practical purposes corrosion does not occur at all in most environments.

A useful article turned to junk as a result of the force of the second law of thermodynamics. Photo: istockphoto.com/robas

However, there are times when we see rust on stainless surfaces and we know that something has gone wrong; the passive film has not done its job. This usually happens on a stainless without Mo in the presence of a strong salt, like sodium chloride, or a strong acid. (Think of those unsightly rust spots that form on your inexpensive stainless steel utensils when you wash them in an automatic dishwasher.) Although chromium is mandatory for any stainless steel recipe, adding Mo to the alloy strengthens the protective effect of the chromium oxide passive film. This is why Type 316 stainless steel (S31600, EN 1.4401) containing 17% chromium and 2% molybdenum is much more resistant to salt-laden environments than Type 304, stainless steel (S30400, EN 1.4301) containing 18% chromium and no molybdenum.

The role of molybdenum – a mystery

Surprisingly, no one is quite sure why Mo is so helpful to the chromium oxide passive film. We do know that the film contains a small amount of Mo. Molybdenum might further retard the transfer of atoms across the film, reducing the general corrosion rate.

General corrosion and pitting on steel. Photo: istockphoto.com/sandramo

We could speculate that molybdenum might help to prevent defects in the film because it is very effective in preventing pitting (highly localized corrosion). Other environmental factors such as salt content further complicate our understanding of the phenomenon to the extent that Mo might play a different role in different circumstances. New scientific studies continue to yield new insights, but to date offer no comprehensive explanation. However, from a practical standpoint, the exact reason behind the behavior is less important than figuring out how to exploit it.

Molybdenum for improved corrosion resistance

There is copious experimental evidence showing that adding Mo to a stainless steel improves the steel's resistance to rust and pit formation. Thus, many manufacturers use Mo in their alloys. Figuring out what degree of alloying will produce steel with the most desirable properties for a specific application and environment is a fine balancing act. As always, cost is a consideration, so not all stainless steels will contain Mo. Nevertheless, Mo is in many of our most corrosion-resistant stainless steels. A recent count identified more than fifty commercial stainless steel alloys that use from 0.5 to 7% of Mo for improved corrosion resistance. Molybdenum obviously does its job very well every day, keeping many industrial plants free of corrosion in extremely aggressive environments, and our cities and homes looking bright and shiny. In fact, after its use in alloy steels, molybdenum in stainless steels represents the largest tonnage application for molybdenum. The second law of thermodynamics certainly is a strong supporter of the molybdenum industry! (bh)

IMOA reaches new heights!

The city of Cusco in Peru was the venue of IMOA's 22nd Annual General Meeting (AGM) and a huge vote of thanks is due to the hosts, Southern Copper Corporation, who could not have chosen better than this historic place. This eagerly anticipated event in the archaeological capital of the Americas drew 140 delegates from 67 companies and 19 different countries. In the rarefied atmosphere of the high Andes, delegates discussed issues affecting the molybdenum industry and sampled the cultural splendours of Peru – and we are not just talking about Pisco Sour!

Pisco Sour was dispensed "off-camera"

Victor Perez (Codelco), in his final year as President of IMOA, opened the proceedings by thanking the Executive Committee and the Secretariat for their unwavering support during his tenure. He went on to review the strengths of the Association and benefits of membership. Not the least of these was the ability of members to act collaboratively in the environmental and regulatory arena to achieve goals that would be beyond the reach of companies acting alone. Team work, he asserted, was the pillar of IMOA's success. As an example, Perez cited the extraordinary effort made by the Association's technical committees over the past four years, culminating in the registration of eleven molybdenum substances under the REACH legislation. He said that beyond the immediate imperative of compliance, this "unique compilation and development of information on the physico-chemical, environmental and human health characteristics of our products will remain as a core of knowledge and data that will serve industry in many regulatory fronts and scenarios in the years to come". In other regulatory jurisdictions IMOA had, especially in relation to water quality standards, encountered "challenges that demanded sound scientific data and a sensible approach to the corresponding authorities". He congratulated the HSE and REACH teams on their productive work.

Turning to promotion, Perez commended the work of the market development committee. He highlighted IMOA's first ever international seminar on applications of molybdenum in steels. The seminar was held in Beijing in June 2010 to advance the concept of energy and resource savings through the increased use of high-strength steels. He also noted that, through an increasing focus on research projects with leading companies and organisations around the world, IMOA was moving beyond mere knowledge transfer to knowledge generation. The revision of the IMOA classic "Practical Guidelines for the Fabrication of Duplex Stainless Steels" in collaboration with ISSF and Euro Inox, and a similar manual for fabricating with austenitics, were two further important achievements during 2010.

In promoting molybdenum in new and existing markets, ensuring continued market access through dialogue with regulators, and maintaining an unrivalled knowledge database about the metal's properties and uses, IMOA had established itself as the "voice of the molybdenum industry" Perez said.

Members expressed their thanks to Mr. Perez for his unstinting service during his three years at the helm of IMOA, and the incoming President, Mark Wilson (Thompson Creek Metals), was warmly welcomed.

Rounding off the week's events, members turned to cultural pursuits by visiting the ancient Inca city of Machu Picchu. The 2011 AGM will convene in the lower altitude, less ancient, but equally fascinating city of Pittsburgh, Pennsylvania, September 14 and 15.

Outgoing President, Victor Perez (left)