Molybdenum in Power Generation

Supercritical and Ultra-supercritical Power Plants

Molybdenum’s contribution to sustainable development in:

- Stainless steels
- Alloy steels
- Superalloys
- Cast iron
- Mo metal
- Chemicals
Raising efficiency from 35% to 50% is estimated to lower CO2 emissions by around 40% (Figure 2).

How molybdenum can help

Raising steam temperature is the most effective way to increase efficiency. However, higher temperatures can only be sustained with suitable boiler materials. If a material is exposed to high temperature and pressure for extended periods, it will 'creep', an initially slow deformation which accelerates over time and eventually destroys the component. A boiler material requirement is that it is able to withstand a stress of 100 MPa at the operating temperature for at least 100,000 hours.

Molybdenum makes an important contribution to sustainable development as a metal, as an alloying element, and as a constituent of chemical products. IMOA’s ‘MoRE FOR LESS’ case studies explore, in more depth, how molybdenum is contributing to sustainable development, a pattern of growth in which resource use aims to meet human needs while preserving the environment.

In particular we will look at how a specific use or application is contributing to the three pillars of sustainability:

- Environmental performance, resource use, energy efficiency & production and recycling
- Supply chain, lifecycle and materials performance
- Health, safety and wellbeing

This case study examines the use of molybdenum in steels and superalloys in fossil fuel power plants. By increasing high temperature strength and resistance to chlorine-containing flue gases, molybdenum enables supercritical and the new generation of ultra-supercritical power stations to run at higher temperatures and pressures, thereby increasing efficiency and reducing CO2 emissions from current and future coal-fired electricity generation.

The Challenge

Global energy demand continues to increase, especially in countries with fast-growing economies. Renewable and low carbon sources can only cover a limited share of the total global energy need. Fossil fuels, particularly coal, meet the vast majority of the remaining demand. This energy mix is predicted to continue as global demand is expected to double by 2030 (Figure 1). Because coal-fired plants emit the most CO2 per kWh generated, improving their efficiency is essential to minimizing global CO2 emissions.

The Solution

The efficiency of a thermal power plant represents the ratio between the net produced electrical energy and the thermal energy originally contained in the fossil fuel. This ratio can be improved by increasing steam temperature and pressure. Power plants are defined as subcritical, supercritical and ultra-supercritical (USC) depending on the temperature and pressure in the steam circuit. On a global basis, the average efficiency of coal-fired power plants is currently below 35%. State-of-the-art supercritical and USC power plants achieve efficiencies of around 45%, while future 700°C technology is predicted to further increase efficiency to over 50%.

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Figure 1: Expected global development of primary power generation. Source: World Energy Council 2010

Figure 2: Impact of boiler technology on thermodynamic efficiency and CO2 emissions. Source: Vallourec
In addition to high stress and temperature, the operating environment in the boiler is corrosive. Steam oxidation on the inside and flue gas corrosion on the outside of boiler tubes becomes more aggressive as temperature increases. Thus the high-temperature corrosion resistance of the material is also a crucial property.

Molybdenum is an important alloying element in such materials as it improves resistance to creep and, in the case of nickel alloys, high-temperature corrosion.

Ferritic steels are typically alloyed with molybdenum, providing sufficient creep strength up to 500°C operating temperature. These steels are the most economical in this line-up and are widely used in sub-critical conditions.

Bainitic and martensitic steels offering higher creep strength have been developed for operation at temperatures above 500°C. These steels contain an increased amount of molybdenum and other alloying elements as well as higher additions of chromium, providing superior corrosion resistance. Molybdenum assists the formation of the strong bainitic or martensitic microstructure. The temperature limit of steels in this group is reached at 650°C.

Austenitic stainless steels are used between 600 and 670°C. Traditionally these steels are molybdenum-free. However, some new grades contain up to 6% molybdenum to expand the usefulness of these steels to 700°C.

Nickel-based alloys such as the modified alloy 617 or alloy 263 are preferred materials for temperatures exceeding 700°C. They have sufficiently high creep strength and excellent resistance to steam-side oxidation and fire-side corrosion. Molybdenum alloying particularly improves corrosion resistance against chlorine-containing flue gases and ashes. The trend of co-firing coal with biomass in various amounts will lead to even more aggressive environments with high concentrations of chloride salt deposits on the tubes. Nickel-based alloys are by far the most expensive materials in this comparison and are therefore reserved for the most demanding conditions where nothing else will work.

Some examples of components, indicative operating temperatures and suitable materials, as well as their molybdenum content, are shown in Table 1.

### Table 1: Operating temperature, molybdenum content and typical grades and tonnages in steam generating boiler section components.

<table>
<thead>
<tr>
<th>Component</th>
<th>Typical temp °C</th>
<th>Type of steel &amp; typical Mo content</th>
<th>Typical grades and tonnages* per boiler</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hot steam and collector pipes, heat exchanger, valves</td>
<td>530–560</td>
<td>Creep resistant ferritic, 0.25–0.60% Mo</td>
<td>15Mo3, 16Mo3, 13CrMo4-5 (2000 tonnes)</td>
</tr>
<tr>
<td>Membrane walls</td>
<td>520–550</td>
<td>Creep resistant ferritic/bainitic, 1% Mo</td>
<td>10CrMo9-10, 7CrMoVTiB10-10 (1500 tonnes)</td>
</tr>
<tr>
<td>Superheater, reheater</td>
<td>550–650</td>
<td>Creep resistant ferritic/martensitic, 1% Mo</td>
<td>X10CrMoVNb9-1, X10CrWMoVNb9-1, X11CrMoWVNb9-1-1, (T/P91, T/P92, E911), higher Cr variants X20CrMoV11-1 (1000 tonnes)</td>
</tr>
<tr>
<td>Superheater, reheater</td>
<td>600–700</td>
<td>Creep resistant austenitic CrNi, residual Mo</td>
<td>X10CrNiCuNb18-9-3, X6CrNiNbN25-20, X8CrNi19-11, (304HCu, 310N, 347HF6) (500 tonnes)</td>
</tr>
<tr>
<td>Superheater, reheater</td>
<td>700 and above</td>
<td>Creep resistant nickel-based alloys, 6–9% Mo</td>
<td>Alloy 617, alloy C-263 (500–3000 tonnes)</td>
</tr>
</tbody>
</table>

* Tonnages based on a typical 3000 tonne boiler
Molybdenum is a key element in technologies for the sustainable use of coal employing an optimised combination of ‘clean coal’ and Carbon Capture and Storage (CCS) technologies. Typical reductions in efficiency of power plants with CCS technology of between 8 and 12% can be partially offset by increased efficiency in a supercritical or USC power station. Molybdenum-containing nickel-based alloys allow co-firing of biomass and waste. Molybdenum-alloyed steels contribute to the profitability of coal-fired power generation, securing baseload capacity and helping to avoid blackouts. Molybdenum-containing steels and nickel-based alloys increase durability, reduce maintenance and conserve resources. Tube production includes established internal and end-of-life scrap recycling with specifically sorted scrap helping to preserve valuable alloying elements like molybdenum. USC power plants offer a sustainable solution to meeting fast growing energy demand in developing economies.

**Summary**

The majority of energy demand in years to come is likely to be met by coal-fired power stations. In order to limit emissions from increased demand, especially in developing economies, the efficiency and flexibility of coal-fired plants must be increased. Molybdenum has an important function as an alloying element in providing sufficient strength at high operating temperatures and protecting components from high temperature corrosion involving chlorides.