

APPLICATIONS OF MOLYBDENUM  
IN  
ENVIRONMENTAL AND HUMAN  
HEALTH PROTECTION



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# "Applications of Molybdenum in Environmental and Human Health Protection"

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FRONT COVER CAPTION

As a shining example of the corrosion resistance of molybdenum-containing stainless steel, the condition of rigging from a sailing-boat contrasts sharply with other debris in a severe sea-water environment.

## SUMMARY

Molybdenum plays a vital part in everyday life, particularly in relation to many aspects of the protection of human health and the environment.

The toxicity of molybdenum is low, reducing concerns about the presence of trace amounts in water and soils which may enter the human food chain. Further, this low toxicity enables molybdenum to play a significant part in lubricants used for food processing machinery, minimising the consequences of accidental contamination.

There has been much concern about the generation of fumes when materials such as those used for carpets and furniture, made from artificial fibres, ignite. Molybdenum compounds in certain polymers have been found to be particularly good smoke suppressants.

Molybdenum-containing catalysts are used in the production of petroleum products to remove sulphur, thereby minimising emissions. This applies not only to the internal combustion engine but also to gas turbines, large combustion plants for power generation and fired heaters in the chemical, petrochemical and process industries.

Molybdenum plays a most important part in processes developed to treat pollutants, such as the desulphurisation of flue gases generated by combustion of sulphur-containing fossil fuels and the cleaning of gases from the incineration of municipal and other wastes. Here, full advantage is taken of the classical role of molybdenum in enhancing the corrosion resistance of stainless steels and nickel base alloys to withstand extreme conditions of corrosion attack.

Cost effective applications of molybdenum-containing materials are demonstrable, taking advantage in design of inherent characteristics of strength, corrosion resistance and integrity.

## INTRODUCTION

In order to protect the environment and human well-being, prevention and minimisation of pollution is essential.

The important principles involved in a considered approach to integrated pollution control are to:-

- prevent pollution at the source, for example by the use of molybdenum catalysts to remove potential pollutants;
- minimise risk to human beings and the environment, for example by encapsulating radioactive wastes in molybdenum stainless steel containers;
- apply advanced technology with best practical options, for example by taking full advantage of the contribution of molybdenum to the enhanced properties of metallic materials.

Most pollution control legislation permits application of advanced technical solutions and it is here that molybdenum-containing materials play an increasingly important part.

# 1.

## THE PART PLAYED BY MOLYBDENUM WITH PREVENTION AND MINIMISATION OF POLLUTION.

Molybdenum plays a major part in achieving the aims of prevention and reduction of pollution.

### 1.1

#### Toxicity and Ecotoxicity of Molybdenum Compounds

Molybdenum compounds in general are of a low order of toxicity, both from observed clinical effects as well as from the histopathologic point of view. In a series of toxicity tests utilising internationally accepted protocols and appropriate laboratory practices, molybdenum-containing compounds such as molybdenum oxide, ammonium dimolybdate and sodium molybdate were found to be non-toxic (based on the European Union criteria for harmful substances) following acute oral, inhalation and dermal exposures. Likewise, these materials were found to be non-irritating to the skin and eyes and non-sensitising.

Ecotoxicity testing showed pure molybdenum oxide, ammonium dimolybdate and sodium molybdate to be non-toxic to fish and daphnids following acute exposure. Algal growth was inhibited only by ammonium dimolybdate, probably due to the ammonia component rather than the presence of the molybdate ion(1).

### 1.2

#### Molybdenum Compounds which Minimise Risk of Unavoidable Contamination or Pollution

Molybdenum and most molybdenum compounds are inherently safe and non-toxic and may be used in a wide range of applications such as lubricants, catalysts, corrosion inhibitors and smoke suppressants to make a positive contribution to environmental well-being.

### 1.2.1

#### Lubrication

Many industrial processes demand that equipment functions under conditions which can cause breakdown of fluid film lubricants. In the case of food processing, avoidance of contamination is most important.

Molybdenum disulphide is an important, well established lubricant with unique characteristics (Fig.1). It is used primarily to reduce wear, friction and to sustain lubrication under boundary sliding conditions. It is an excellent high-temperature lubricant which is stable in vacuo or an inert atmosphere to a temperature of 1200°C and about 300°C in air. Significantly toxicity levels are extremely low for use in certain sensitive applications. As an example, the United States Food and Drug Administration has authorised the use of a molybdenum disulphide-containing lubricant in bakery oven chains where incidental food contact is a possibility.

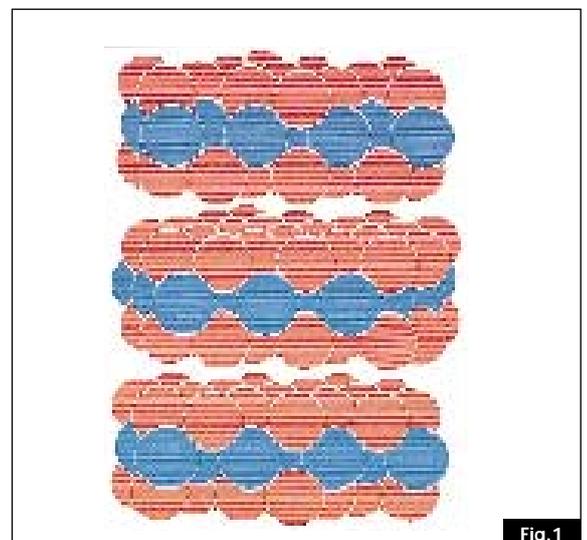


Fig. 1

"Three layers of the molybdenum disulphide structure drawn from X-ray diffraction data. Sulphur atoms are red and molybdenum atoms are blue. Within each layer, strong S-Mo-S bonds resist penetration by surface asperities. Between the layers, weak S-S bonds allow easy sliding of the layers resulting in low friction and lubricity."  
(*IMOA "Molybdenum", p17*)

Molybdenum disulphide is frequently applied to surfaces on assembly to provide short term lubrication of engines and gearboxes to prevent galling prior to supply of lubricant from pressure fed systems(2). It is also incorporated into rubbers, plastics and powder metal components to impart life time self-lubrication and in greases employed in mining and transportation to provide back-up lubrication should a grease deplete or thermally degrade(3).

In ultra-fine form, molybdenum disulphide is suspended in lubricants such as motor oils acting as an extreme pressure lubricant. An important use is the improvement of fuel economy in vehicles and the contribution to environmental protection by reduction of exhaust pollutants(4).

1.2.2

### Removal of Pollutants by the Use of Molybdenum Catalysts

Catalysts, including those containing molybdenum, have been used effectively for many years by the petroleum refining industry(5). The 1990 Clean Air Act in the United States and comparable legislation in Japan and Europe have led to the increasing world-wide use of hydroprocessing catalysts for environmental protection. As oil reserves are progressively depleted and the heavier oil fractions are increasingly used, it is evident that the sulphur content of the remaining crude oils will progressively increase. Further, many new discoveries over the last decade have had inherently higher sulphur content. Demands for reformulated gasolines to minimise poisoning of automotive exhaust catalysts and increased use of oil prompt further development of the molybdenum catalysts.

1.2.3

### Corrosion Inhibition

Inorganic molybdates are widely employed as corrosion inhibitors, for example in motor vehicle cooling systems. Molybdates are anodic inhibitors, precipitating escaping metal cations as complex molybdate species to block anodic sites and strengthen developing metal oxide films. Molybdates inhibit corrosion of more ferrous and non-ferrous metals over a wider pH range than almost any other inhibitor; the molybdate, however, has very low toxicity(5). This is significant in that corrosion inhibition is applied to a wide range of uses where discharges to waste water systems are necessary. Open cooling systems include those associated with power generation, manufacturing operations, metals production and chemical processing. Through the use of molybdate inhibitors, disposal of cooling media from open as well as closed loop systems for refrigeration and humidity control equipment is, therefore, less hazardous.

1.2.4

### Smoke Suppression

Molybdenum compounds have been found to be particularly good smoke suppressants for rigid and plasticized PVC systems. Molybdenum trioxide and proprietary molybdate compositions work in the solid phase of these plastics, increasing char formation and thereby substantially reducing the volume of smoke generated and simultaneously providing fire retardancy(5).

## 2.

# THE INFLUENCE OF MOLYBDENUM IN MATERIALS FOR CONTAINMENT AND PROCESSING OF POLLUTANTS

Molybdenum, as an alloying element in many materials but notably in stainless steels and nickel base alloys, enhances corrosion resistance for the safe containment and transport of many aggressive industrial processes and products. The various forms of corrosion to which metallic materials may be susceptible are well documented(6).

### 2.1

#### Effects of Alloying in Stainless Steels and Nickel Alloys

In order to achieve the critical service demands made of metallic materials in most aggressive conditions experienced with containment of pollution and pollution control systems in various forms, excellent corrosion resistance is required.

Molybdenum is very effective in stabilising the passive metal oxide film characteristic

of the stainless steels and nickel base alloys provided by the presence of chromium, together with nickel and nitrogen, to impart structural stability and facilitate fabrication.

Even the high alloy content "super" austenitic stainless steels may have inadequate performance in the very severe corrosion conditions encountered in environmental production equipment, and the use of higher molybdenum-content nickel base alloys is necessary.

Significantly, nickel base alloys can accommodate larger amounts of alloying elements such as chromium, molybdenum and tungsten in solid solution than the iron base austenitic stainless steels. Chromium plays an important part in imparting improved resistance to oxidising media, whilst higher molybdenum content substantially improves resistance to non-oxidising acids and also markedly

UNS NUMBER (Material Designation)(a)	Cr	Ni	Mo	Fe	W	Cu	C	Other
S31603 (316L)	17	12	2.2	BAL	—	—	0.03	0.05N
S31703 (317L)	19	13	3.2	BAL	—	—	0.03	0.05N
S31725 (317LM)	19	15	4.2	BAL	—	—	0.03	0.05N
S31726 (317LMN)	19	15	4.2	BAL	—	—	0.03	0.15N
S31803 (Alloy 2205)	22	5.5	3	BAL	—	—	0.03	0.15N
S32550 (Alloy 255)	25	5	3	BAL	—	2.0	0.03	0.17N
6% Mo Stainless Steels	20	18-25	6	BAL	—	0.75-1.00	0.02	0.15N-0.25N
S31266 (Alloy B66*)	24.5	22	5.6	BAL	2	1.5	0.02	0.45N
S32654 (Alloy 654SM0*)	24	22	7.3	BAL	—	0.5	0.015	0.50N
N06625 (Alloy 625)	21.5	61	9	4	—	—	0.05	3.65Cb + Ta
N10276 (C 276)	16	57	16	5	3.8	—	0.01	—
N06022 (Alloy C 22* Alloy 622*)	22	59	13	3	3.0	—	0.01	—
N06059 (Alloy 59*)	23	59	16	1	—	—	0.01	—
N60200 (Alloy C 2000*)	23	57	16	3	—	1.6	0.01	—
N06686 (Alloy 686*)	20.5	57	16.3	1	4.0	—	0.005	—

\* Alloy C 22 and Alloy C 2000 are trademarks of Haynes International.

\* Alloy 622 and Alloy 686 are trademarks of Inco Alloys International.

\* Alloy 59 is a trademark of Krupp-VDM.

\* Alloy B66 is a trademark of Creusot-Loire Industrie.

\* Alloy 654SM0 is a trademark of Avesta-Sheffield.

(a) From "Metals and Alloys in the Unified Numbering System", Society of Automobile Engineers, Warrendale, Pa. USA.

improves the pitting and crevice corrosion resistance of the nickel base alloys. These alloys are most important in modern industry because of their ability to withstand a wide range of most severe operating conditions. At the same time they are readily formed and welded, enabling them to be used easily and cost effectively.

The enhanced performance of the molybdenum-containing materials (Table 2) which exhibit very high resistance to pitting in oxidising chloride media is important in pollution control equipment.

2.2

## Selection and Performance of Materials

Corrosive environments are frequently very complex. For example, the combustion products from the incineration of wastes containing plastic materials may generate aggressive acid mixtures contaminated with

fluorides and chlorides. Generally the higher the molybdenum and chromium content, the better the performance of the alloys in such acid mixtures.

A practical comparison of potential performance of molybdenum-containing stainless steels and nickel base alloys is possible by using, as an indication, an index known as the Pitting Resistance Equivalent calculated in accordance with accepted formulae (7). Commonly adopted are

$$\text{PREN} = \%Cr + 3.3 \times \%Mo + 16 \times \%N$$

or when tungsten is also present

$$\text{PRENW} = \%Cr + 3.3 \times \%Mo + 1.65 \times \%W + 16 \times \%N$$

A list of materials (Table 3) which may be utilised for pollution control and process equipment, is shown in ascending order of PRENW.

**UNS NUMBER  
(Material Designation)(a)**

$$\text{PRENW} = \%Cr + 3.3 \times \%Mo + 1.65 \times \%W + 16 \times \%N$$

S31603 (316L)	25
S31703 (317L)	30
S31725 (317LM)	34
S31726 (317LMN)	35
S31803 (Alloy 2205)	34
S32550 (Alloy 255)	38
6% Mo Stainless Steels	44
S31266 (Alloy B66)	
N06625 (Alloy 625)	51
S32654 (Alloy 654SMO)	
N06022 (Alloy C-22, 622)	70
N10276 (Alloy C-276)	75
N06059 (Alloy 59)	76
N06686 (Alloy 686)	81

This is not intended to be an exhaustive compilation.

There have been further developments with alloys since the above table was published.

For example:

S31266 (ALLOY B66)	54
S32654 (ALLOY 654 SMO)	56

(a) From "Metals and Alloys in the Unified Numbering System", Society of Automobile Engineers, Warrendale, Pa. USA.

PITTING RESISTANCE EQUIVALENT NUMBERS (PRENW) FOR VARIOUS MOLYBDENUM-CONTAINING MATERIALS (7)

Table 3

2.2.1

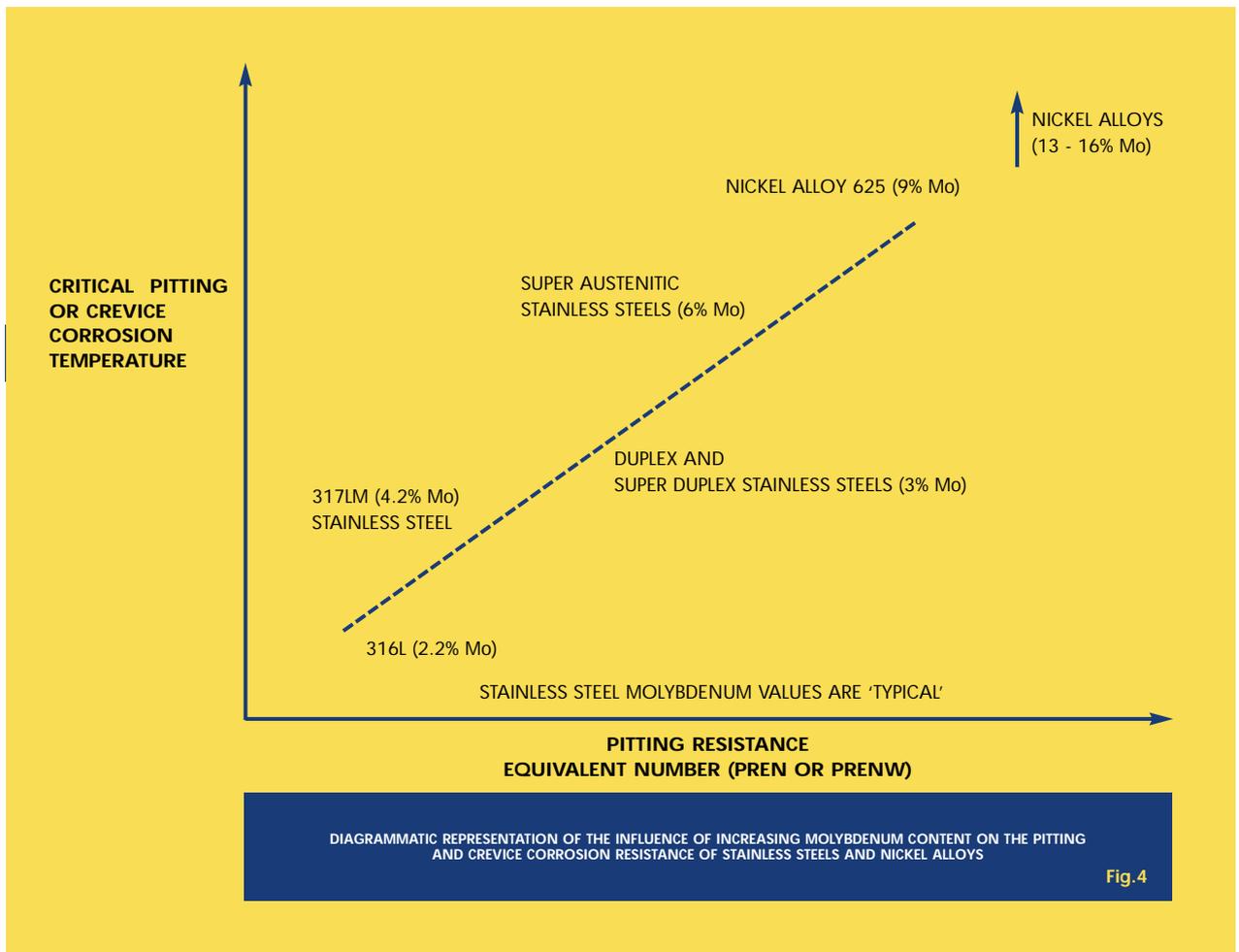
**Performance of Stainless Steels**

With chromium and nickel contents of about 18% and 8% respectively, stainless steels are widely known and familiar, not least in domestic use. Developments of more highly alloyed materials essentially involve the addition of molybdenum and nitrogen with increased chromium and nickel contents. These additions are of decisive importance across a broad composition range in providing the steels (and also the nickel base alloys) with a high degree of resistance to pitting and crevice corrosion, the significance of which is indicated by reference to the PREN or PREN<sub>w</sub>(Fig.4).

In conjunction with the benefits derived from careful selection of a suitable grade of

material with appropriate molybdenum content, fit for purpose, the performance of materials in service can be significantly enhanced by careful attention to design and fabrication.

In welded assemblies, the joint formed is of necessity a cast structure within which a significant degree of micro-segregation of alloying elements can occur. In addition to control of heat input to minimise such effects, it is common practice to use wherever possible welding consumables with alloy content higher than that of the parent metal to minimise the possibility of preferential corrosion attack of the weld. Elements of importance are chromium and molybdenum and these are increased appropriately with due regard to practical service conditions, weldability and cost.



2.2.2

### Performance of Higher Alloyed Nickel-Chromium-Molybdenum Materials

These materials combine the good resistance of nickel-molybdenum alloys under reducing conditions with the superior resistance of nickel-chromium alloys under oxidising conditions, whether as highly alloyed “super” austenitic or duplex stainless steels or as nickel base alloys. All provide wide ranging resistance in wet corrosion conditions in the presence of chlorides and oxidising iron and copper salts, together with good resistance to pitting and crevice corrosion. Resistance to reducing acids is achieved with higher molybdenum-content nickel alloys (Table 2) which, coupled with increased chromium, also provide greater resistance to severely oxidising media.

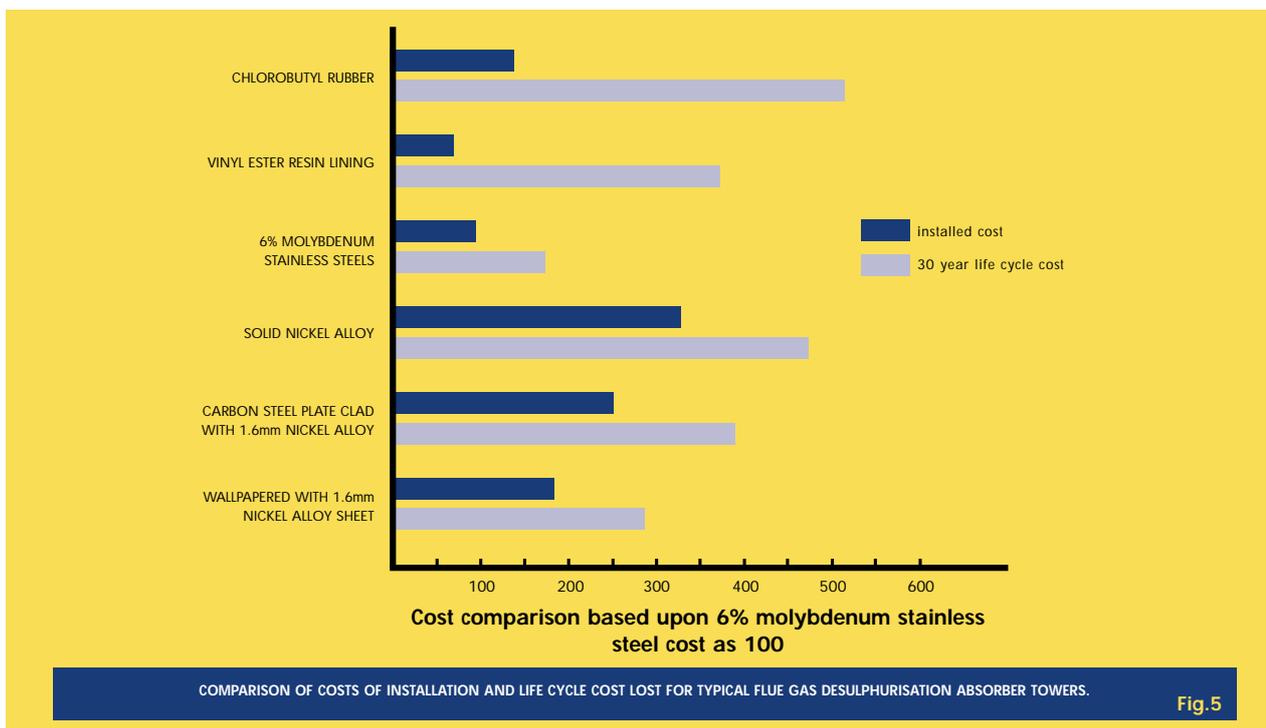
are adjusted to a consistent time basis and are combined into a single measure of cost-effectiveness to facilitate the comparison of alternative systems or materials(8). As extensive service experience has shown that flue gas handling equipment fabricated with molybdenum-containing materials can provide significant benefits by the reduction of failures, they are increasingly substituted for non-metallic materials. However, the initial higher cost of installation has discouraged consideration of the metallic option, particularly in the emerging eastern European economies.

2.3

### Life Cycle Costing

Materials engineers and designers increasingly employ life cycle cost analysis in determining the viability of equipment design and construction. Individual costs

Comparisons of the installed costs and life cycle costs for non-metallic and metallic materials for Flue Gas Desulphurisation (FGD) absorber towers are presented (Fig.5). The use of specific molybdenum-containing materials and product forms can be seen to offer lower life cycle costs than those for non-metallic materials, a fact which has resulted in the preferred use of molybdenum-containing materials for a majority of the recent FGD system installations in North America and Europe(9)(10).



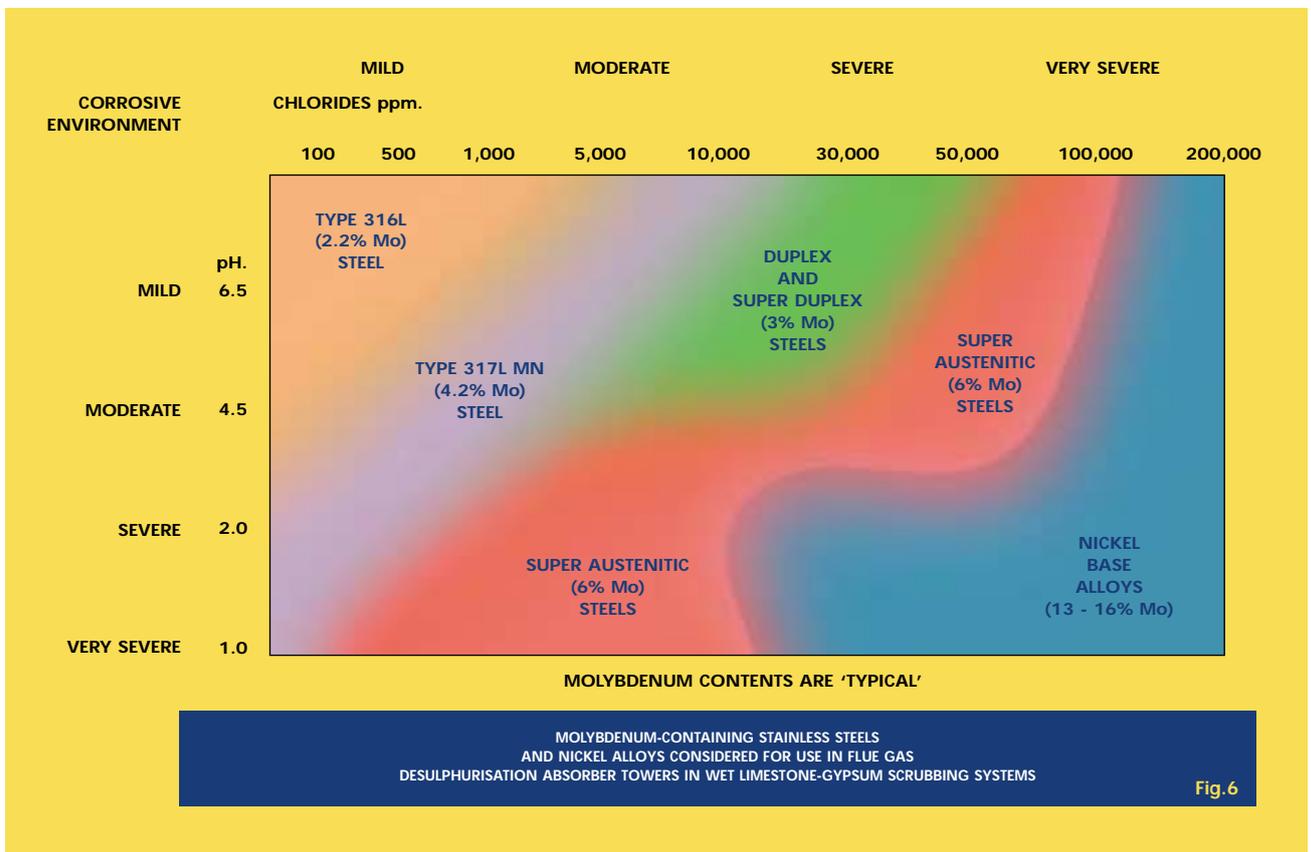
2.4

## Corrosion Performance versus Material Cost

Where pollution cannot be avoided, or totally controlled at the source, treatment of emissions is necessary. Many processes involve aggressive conditions so that materials considered for use in pollution control equipment are generally the molybdenum-containing austenitic or duplex stainless steels and nickel base alloys, taking advantage of their superior corrosion resistance.

process equipment, ensuring potentially low maintenance costs, together with high availability of equipment over many years of use.

Selection of the appropriate grade is determined by the need to minimise cost by utilising the least possible amount of alloying elements, balanced against the risk of corrosion damage(Fig.6). With appropriate selection and application, the molybdenum-containing materials offer cost effective solutions to corrosion problems in a wide range of industrial and



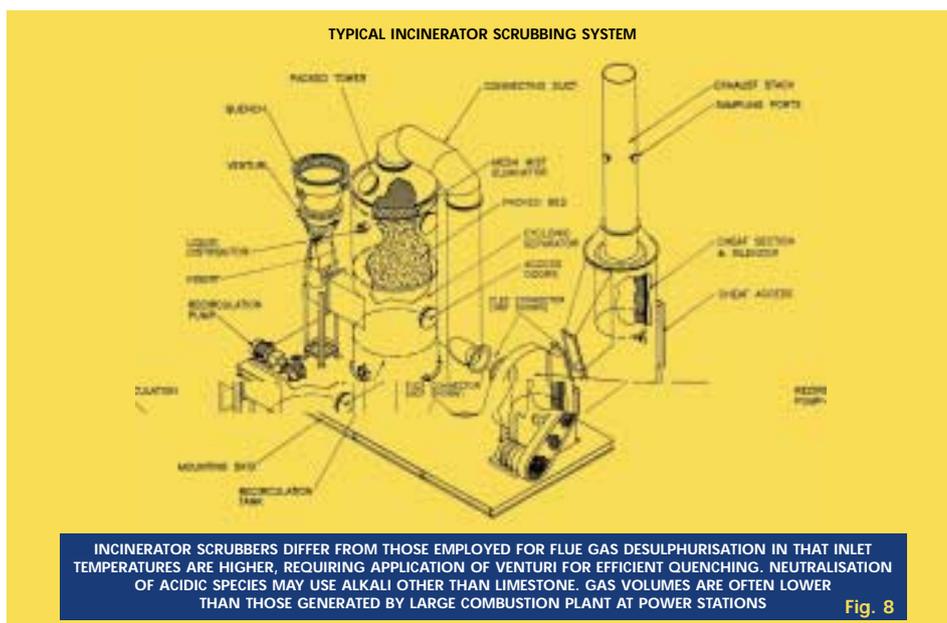
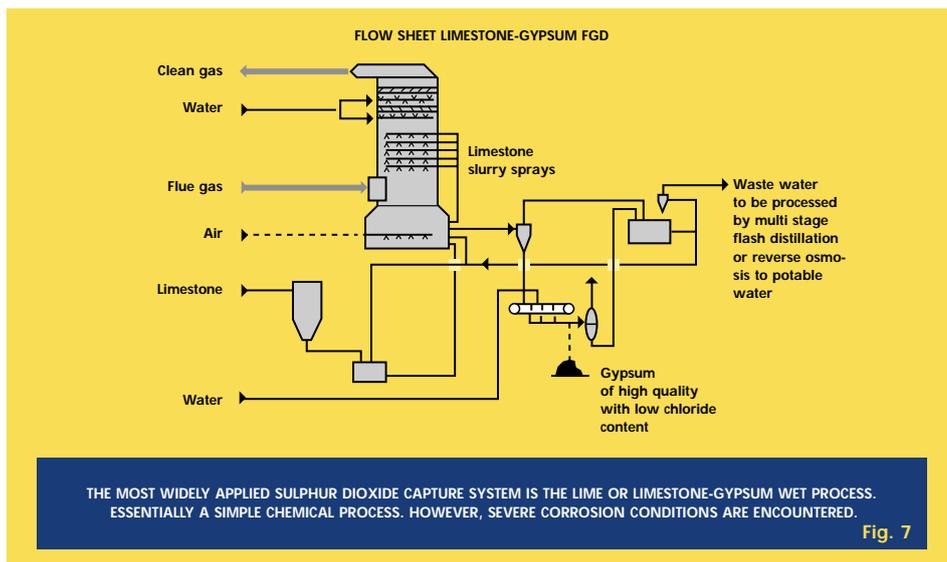
### 3.

## APPLICATION OF MOLYBDENUM-CONTAINING NICKEL ALLOYS AND HIGH ALLOY STAINLESS STEELS

It is significant that the molybdenum-containing nickel base alloys and the special high alloy (or "super") stainless steels are finding increasing application in chemical plants and power generation, particularly when consideration is given to the demands of long life and cost effective design of pollution control equipment to comply with legislation limiting emissions.

It is appropriate to consider them as a single group of materials as the increase in molybdenum content progressively improves resistance to general corrosion attack. Corrosion by mixed acids

contaminated with other species such as chlorides and fluorides, which accelerate attack, is of particular significance, and careful choice is necessary to optimise performance at least cost from the range of molybdenum-containing materials made available. In general, the material also requires increased nickel content to resist higher chloride ion concentration and lower pH (Fig.6). The more highly molybdenum alloyed materials are widely used to prevent corrosion by contaminated sulphuric acid in flue gas scrubbers, utilised to clean gases from power station boilers (FGD)(Fig.7) and incinerators (Fig.8).



3.1

## Air Quality

Good air quality is essential for human health and the well-being of the environment as a whole.

Governments have responded decisively by the introduction of legislation demanding reduction of emissions. Equipment to remove sulphur dioxide from flue gases is being widely introduced with parallel action to minimise emission of oxides of nitrogen (NO<sub>x</sub>).

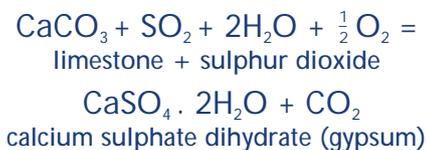
3.2

## Materials Utilisation in Flue Gas Desulphurisation and Incineration Scrubbing Systems

There are numerous systems differing markedly in design concept and operating conditions so that a generalised approach to the subject is appropriate.

The most widely employed FGD system is the wet limestone-gypsum process in which raw flue gas from combustion units is conditioned to an appropriate temperature and then the sulphur dioxide and acidic gases such as hydrogen chloride are neutralised and captured by a commonly available alkali, limestone (calcium carbonate) (Fig.8). Whilst acknowledged as a simple process, with reactions taking place adiabatically at about 50-65°C, quite severe corrosion conditions can occur.

The reaction, simply stated, is:-



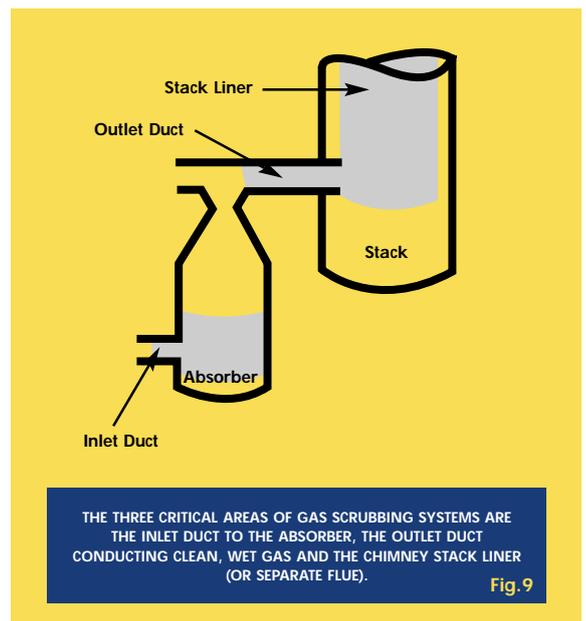
A great deal of practical experience and research into material suitability has enabled recommendations to be established and to make cost effective choice possible (Figs.5&6).

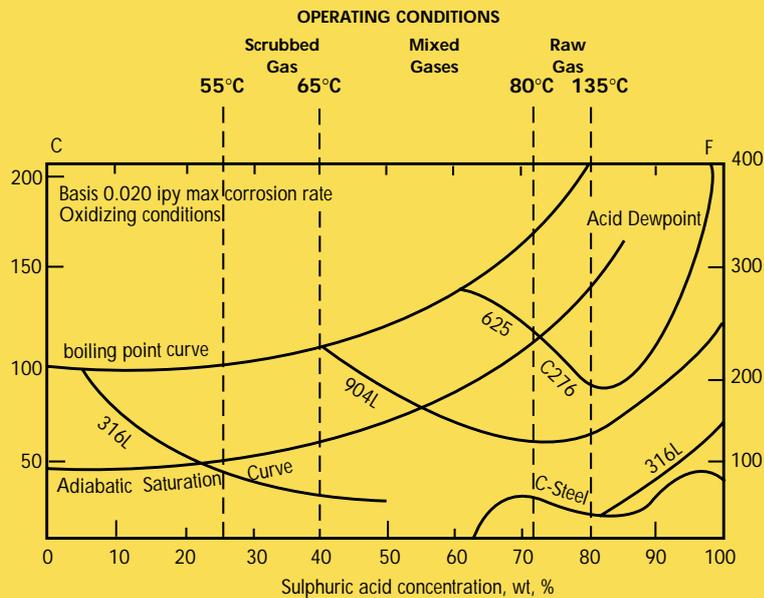
A disadvantage of the wet scrubber is the requirement for waste water treatment facilities. Regulatory authorities increasingly demand systems that do not discharge untreated process water resulting in progressive increase of impurities, such as chlorides, in process streams. The generation of more aggressive conditions requires use of higher corrosion resistant molybdenum-containing steels and alloys for cost effective, reliable and durable water treatment systems utilising multi-stage flash distillation or reverse osmosis (Fig.8).

3.2.1

## Materials of Construction

Wet scrubbing systems are exposed to an aggressive environment leading to corrosion, erosion and abrasion. The flue gas path from the inlet of the absorber to the chimney stack (Fig.9) must be protected against acid precipitated on adiabatic cooling (Fig.10) and saturation of the gas.





ADIABATIC SATURATION CURVE SHOWING  $H_2SO_4$  CONCENTRATION FOR VARIOUS TEMPERATURES AND OPERATING CONDITIONS IN FLUE GAS DESULPHURISATION PLANT. THE EFFECTS OF PARTIAL BY-PASS AND MIXING RAW AND SCRUBBED GASES ARE INDICATED.

Fig.10

### 3.2.2

### Cost Effectiveness

Non-metallic linings such as resins, vinylesters, polyesters and fluor-elastomers were attractive as materials for wet scrubbing systems such as FGD because they offered a lower initial cost when employed for the protection of the carbon steel structures. However, numerous failures of non-metallic linings by blistering, debonding and wear from abrasive slurries have been reported. High temperatures can damage or destroy non-metallic linings which are known to ignite with catastrophic consequences. Rubber linings offer good resistance to abrasion, but close attention to product specification and careful application are required to assure acceptable quality of lining.

Protecting carbon steel structures with thin molybdenum-containing nickel alloy by “wallpapering” (typically 1.6mm or 1/16th inch thick)(Fig.11) or utilising clad plate (where nickel-molybdenum chromium alloys are explosive or roll bonded to carbon steel substrate) are options considered for the wet/dry interface at the hot gas inlet to the absorber tower and other critical areas, to minimise the cost of construction.

The nickel-molybdenum-containing steels and alloys are noteworthy for their ready fabrication and welding with conventional procedures(11).



Fig.11

Wallpapered clean gas ductwork leading to the base of a chimney, lined with alloy C-276 (16% molybdenum) to replace failed acid resisting ceramic lining. (Public Service of Indiana, Gibson Power Station, USA)



Fig.12

FGD Tower at VEAG power station, Jaenschwalde, Germany. Solid "super" austenitic stainless steel upper section and 16% molybdenum nickel alloy clad plate base, provide excellent corrosion resistance. (Preussag-Noell)

### 3.2.3

#### Lightweight Design

Solid stainless steel construction is used for absorbers where service and cost considerations are satisfied by the use of molybdenum-containing austenitic or duplex grades. Lightweight design concepts using exterior reinforcement have been successfully used for road and rail tankers, permitting reduction in section thickness and cost with increased payload carrying capacity, utilising intrinsically more reliable molybdenum stainless steels to provide assurance to the design

qualification authorities. By turning such tanks through 90 degrees, a vertical vessel is provided with equally attractive weight and cost reduction (Fig.12).

### 3.2.4

#### Cost Reduction

The capital and operating costs of the wet limestone process have been considerably reduced over the past decade with maturing technology. Many of the problems with the first generation systems have been solved, and innovative designs have incorporated numerous advances offering

simpler systems which utilise a single integrated absorber without spare capacity. Significantly, the cost effective utilisation of metallic materials such as the "super" austenitic and "super" duplex molybdenum-containing steels and the nickel alloys now enables the installation of competitive equipment with proven long term durability and reliability.

### 3.2.5 Chimneys

Tall chimneys have largely solved the problem of intense local ground level pollution around factories and power stations where fossil fuels are used in large combustion units.

Metallic lining of the complete stack or of individual flues is becoming established as a beneficial solution to practical problems of chimney design, cost and maintenance.

Molybdenum-containing materials offer cost effective alternatives to the traditional materials used, particularly where greater volumes of condensates are encountered with the lower temperature gases discharged from wet gas-scrubbing pollution control systems.

## 3.3 Water Quality

The provision of potable water in adequate quantity is vital. Legislation to minimise contamination is being enacted to control the release of pollutants generated by industrial processes or as a by-product of other pollution control systems.

### 3.3.1 Purification and Distribution of Drinking Water

There is increasing use made of austenitic stainless steels of standard grades, defined as those having relatively low chromium and molybdenum contents, for water purification and distribution systems of high integrity.

Potable water may be obtained as a consequence of the treatment of discharge from industrial process streams to minimise environmental impact. However, concern has been expressed regarding increased occurrence of microbiologically influenced corrosion (MIC) of stainless steels. The higher molybdenum stainless steels, typically of 6% content, are reportedly free from observed MIC and, therefore, represent a practical engineering solution to problems associated with lower alloy content grades(12). This is an example of molybdenum dealing effectively with the consequential effects of measures introduced to minimise the environmental impact of discharges from pollution control systems.

The processing of contaminated water discharges(Fig.8) by multi-stage flash distillation, or reverse osmosis processes established for desalination, is of increasing interest. These processes utilise molybdenum-containing materials to prevent "taint" of potable water and the degradation of equipment handling increasingly corrosive liquors containing high concentrations of chlorides.

### 3.3.2 Environmental Aspects

The regulation of chemical discharges into the environment is increasing world-wide. In general, although molybdenum (like all other metals) can cause concern when discharged in excessive quantities, the problems encountered are well understood and may be easily corrected.

In waste water, soluble molybdenum compounds exhibit comparatively low levels of toxicity when discharged into fresh or salt water or sewage treatment facilities. Atmospheric discharges of solid pollutants are controlled by filters, cyclones or scrubbers. In the case of flue gas systems for incineration plant or large fossil fuel combustors, particulate discharge is well controlled by wet scrubbing systems.

## 4.

# PREVENTION OF POLLUTION

Wherever possible, it is preferable to remove a potential pollutant at source. As the presence of sulphur is common in most fossil fuels, processes to remove the sulphur will significantly influence the amount of sulphur oxides generated on combustion.

### 4.1

#### Refining Processes

Hydrotreating processes (hydrodesulphurisation and hydrodenitrogenation) are used to reduce sulphur and nitrogen components in organic pollutants. Hydrotreating catalysts commonly consist of molybdenum compounds supported on gamma alumina in combination with cobalt or nickel promoters. In operating conditions Mo-S species form as the active component(13).

The largest use of molybdenum catalysts is in the desulphurisation of petroleum, petrochemicals and coal derived liquids in which organo-sulphur compounds react with hydrogen at the catalyst surface to be removed as hydrogen sulphide. These sulphur reduction processes have a major impact upon air quality. Desulphurisation is employed not only to improve product stability and odour, but most importantly to eliminate sulphur dioxide emission on combustion of fuels.

Current European legislation permits sulphur contents of 500ppm for petrol and 2,000ppm for diesel, with proposals to reduce these to 200ppm and 250ppm respectively by year 2000.

Molybdenum-containing catalysts are also used for a broad range of reactions within the chemical and petrochemical industries, for example hydrogenations ( $\text{MoS}_2$ ), selective oxidations (vanadium, iron, cobalt and bismuth molybdates), epoxidation and polymerisation ( $\text{MoO}_3$ ), etc. (14).

### 4.2

#### Recycling of Catalysts

To minimise impact on the environment, spent hydroprocessing catalyst is removed from the refinery and either regenerated or the metallic content recycled and used, for example in the production of alloy steels.

### 4.3

#### Solid Waste Disposal

Much industrial and domestic waste has been historically dumped at sea or as land-fill. As concern about ocean pollution levels led to a total ban on dumping, demand has increased for land-fill disposal at a time when suitable sites are limited. Incineration, which is particularly appropriate for many hazardous materials such as toxic and clinical wastes, can reduce land-fill demand and at the same time conserve energy by the recovery of heat, utilising molybdenum-containing materials to advantage.

### 4.4

#### Hazardous Wastes Disposal

Encapsulation in molybdenum stainless steel containers for maximum security, or treatment by vitrification (melting to glass-like forms which seal the hazards) utilising molybdenum resistance heating elements, are increasingly undertaken with radioactive wastes and for the removal, transport and disposal of highly contaminated soils.

## CONCLUSION

Molybdenum plays a vital part in numerous processes developed to protect human health and the environment.

Prevention of pollution by the economical treatment of fuels to remove polluting elements at the source is now widely adopted, by advantageous utilisation of the unique characteristics of molybdenum catalysts. The inherent low toxicity of molybdenum and its compounds is increasingly acknowledged for both the control of pollution and minimising the detrimental effects of pollutants.

Cost effective treatment of pollution is facilitated by taking advantage of the beneficial properties and characteristics of a wide range of molybdenum-containing structural materials ranging from the 2.5% molybdenum stainless steels to the 16% molybdenum nickel base alloys. These materials provide ready achievement of durability and reliability with environmental protection equipment subject to most arduous service environments.

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## REFERENCES

1. "Molybdenum in relation to Health, Safety and the Environment," International Molybdenum Association leaflet. 1997.
2. Y.LIN, "Antifriction and Antiwear Characteristics of Molybdenum Dithiophosphate in Engine Oils" Lubrication Engineering 51 , 10, pp 855-860.
3. "Molybdenum" 1992, IMO, pp 17-18.
4. E.R.Braithwaite & A.B.Greene, "A Critical Analysis of the Performance of Molybdenum Compounds in Motor Vehicles", Wear, 46, 2, pp 405-432.
5. Ullmann's "Encyclopedia of Industrial Chemistry, Molybdenum and Molybdenum Compounds", Vol A16, pp 655-698, VCH, 1990.
6. "Glossary of Corrosion Related Terms" Item 37764, NACE, Houston, TX.
7. E.Alfonsson., R.Qvarfort, "Investigation of the Applicability of Some PRE Expressions for Austenitic Stainless Steels" ACOM No1-1992.
8. J.D.Redmond, R.M.Davison, Y.M.Shah, "Life-Cycle Cost Comparison of Alternative Alloys For FGD Components" NiDI Technical Series No. 10 023.
9. R.L.Torstrick, P.F.Ellis, "Materials Selection for Hypersaline FGD Systems: Economics" Proceedings 1992 Air Pollution Seminar, Orlando, FL, 1992.
10. R.E.Avery, W.L.Mathay, W.H.D.Plant, "Utilization of Nickel-Containing Alloys for FGD Systems in North America and Europe" Corrosion '96, Paper 455, NACE, Houston, TX.
11. R.E.Avery, W.H.D.Plant, "Welding And Fabrication of Nickel Alloys in FGD Systems" NiDI Technical Series No.10 027.
12. C.WKovach, J.D. Redmond, "High Performance Stainless Steels and Microbiologically Influenced Corrosion" Proceedings International Congress Conference Stainless Steels '96, Dusseldorf, June 1996.
13. H.Topsoe, B.S.Clausen, F.E.Massoth, "Hydrotreating Catalysts", Springer, 1996.
14. Molybdenum Catalyst Bibliography, Bulletins: C-40, C-54, C-73, C-77, C-96, C-111, C-119, C-130, C-135, C-139.Climax Molybdenum Co, Amax Inc. Greenwich, Conn. 1950-1983.

## List of other IMO publications

### Molybdenum

The Evolution of High Performance Stainless Steels

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THE INTERNATIONAL MOLYBDENUM ASSOCIATION (IMO) was founded in 1989 and has become the focal point of promotional, statistical and technical activities for the worldwide molybdenum industry. Membership is broad based and includes producers, consumers, converters, traders and assayers. IMO's secretariat is based in London.

IMO's main activities currently include:

- promoting molybdenum as a material with superior properties and performance in a wide variety of metallurgical, chemical and other product applications;
- monitoring molybdenum in relation to health, safety and environmental issues; with the increasing amount of legislation in

many countries relating to the use and disposal of metals and metal bearing materials, IMO provides a centralized service including research studies on those issues that may affect the molybdenum industry;

- collecting the industry's most comprehensive historical statistics on world supply and demand of molybdenum products which are distributed to all IMO members on a regular basis;
- organizing meeting and promotional conferences beneficial to the molybdenum industry;
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