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The effect of drag-reducing additives on the rheological properties of silica-water suspensions containing iron(III) oxide and of a typical gold-mine slurry

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SYNOPSIS

Certain polyionic species such as sodium tripolyphosphate are known to enhance the flow properties of silica-based industrial slurries, e.g. gold-mine wastes, by reducing the yield stress. However, this behaviour depends on components other than silica in the slurry, and is not observed with pure silica-water suspensions. The effect can be demonstrated on silica-water suspensions containing up to 10 per cent iron(III) oxide. This paper shows the effects of two additives, sodium tripolyphosphate and XP23/86 (a commercial slurry thinner), that were investigated by use of a specially modified viscometer capable of handling settling slurries. The presence of iron oxide in the model slurry appears to modify the activation energy for the flow process by introducing a term akin to chemical potential, which, in turn, is modified by the presence of drag-reducing additives. Quantitative analysis indicates a relationship between the effect of the additive and the dissociation of its ionizable groups. The results obtained for a typical gold-mine waste are presented for comparison.

SAMEVATTING

Sekere poli-ioniese spesies soos natriumtripolifosfaat is bekend om die vloei-eienskappe van silika-basis industriële slurries te verhoog, bv. goudmynafval, deur die meegeespanning te verlaag. Hierdie gedrag word bepaal deur ander komponente as silika en word nie in suiwer silika-water suspensies waargeneem nie. Die effek kan demonstreer word deur gebruik te maak van silikon-water suspensies wat tot 10 persent yster(III)oksied bevat. Hierdie referaat bepaal die effek van byvoegmiddels, natriumtripolifosfaat en XP23/86 ('n kommersiële slurrieverdunner), wat geondersoek is deur gebruik te maak van 'n gemodifiseerde viskositeitsmeter wat in staat is om afsakkende slurries te hanteer. Dit wil voorkom of die teenwoordigheid van ysteroksied in die modelslurrie die aktiveringsenergie van die vloeiproses verander deur 'n term verwant aan chemiese potensiaal, wat op sy beurt verander word deur die teenwoordigheid van sleur-verminderende byvoegmiddels. Kwantitatiewe analise wys op 'n verband tussen die effek van byvoegmiddels en die dissosiasie van ioniseerbare groepe. Die resultate wat verkry is deur gebruik te maak van tipiese goudmynafval word hier aangebied vir vergelyking.

Introduction

A common problem in many mining operations is the efficient disposal of wastes or tailings, which consist of very fine powders with an average diameter of around 10 to 50 μm. This is normally accomplished by the pumping of the solids as a thick aqueous suspension or slurry, at as high a concentration as the power of the pumps will allow (usually more than 60 per cent by mass), to settling ponds or, better still, to worked-out sections of the mine. The economic efficiency of this process depends on the power requirements for pumping, which, in turn, depend on the concentration, viscosity, and yield stress of the slurry. Certain polyionic species such as sodium tripolyphosphate (NaTPP) are known to reduce the yield stress of concentrated slurries[1], which, in turn, reduces the pumping power required and increases the efficiency of the pumping operation. Such additives enable slurries to be pumped at a much higher concentration of solids, thus reducing the water requirements, which is an important consideration in Southern Africa.

Many mineral slurries consist largely of silica with varying amounts of other materials (e.g. clays, iron(III) oxide, alkaline earth compounds), and it appears to be the presence of these other materials that has adverse effects on the rheological properties of the slurry, causing an increase in yield stress. On the other hand, these materials react with drag-reducing additives such as NaTPP, thus reducing the resistance to flow[2]. Despite the technological importance of this behaviour, no attempts were made until recently to provide a satisfactory mechanistic explanation in quantitative terms that can readily be applied to actual pumping situations.

A possible explanation for this omission is the lack of suitable laboratory equipment for investigations on the type of slurries encountered in the mining industry. Such slurries are fairly coarse suspensions and have a tendency to settle out, making laboratory determinations extremely unreliable, particularly where drag-reducing additives are studied. This was recently overcome by the modification in various ways[3-5] of commercially available viscometers, which keep the slurry in homogeneous suspension, enabling consistent and reliable rheological results to be determined; such equipment is now available at this University.

Most mineral slurries exhibit properties of non-Newtonian pseudo-plastic flow, and are generally shear-thinning; that is, at low shear rates, the resistance to flow

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is high but decreases as the rate of shear increases to a relatively constant value. This resistance to flow at low shear rates is usually interpreted as a yield stress, and the effect of drag-reducing additives is to reduce this yield stress and achieve the same high shear-rate viscosity with much less effort. A simple chemical model, formulated from the chemical analysis of an actual sample of gold-mine tailings, is a coarse suspension of silica containing up to 10 per cent iron(III) oxide or other metal oxides, and this system provides a basic model for the description of flow mechanisms and the effect of drag-reducing additives[6,7].

The purpose of this paper is to report on the experimental and analytical methods that have been developed in the University laboratories for the determination of the relative effectiveness of drag-reducing agents on mineral slurries. The methods are relatively simple and can be carried out with small quantities of material.

Materials and Methods

An essential component of this study was a viscometer capable of handling slurries that tend to settle out. This was achieved by use of a standard Haake RV 100 cup-and-rotor viscometer in which a rotating bowl pitched at 45° to the horizontal was used as the cup, which kept the slurry homogeneous, and into which the viscometer proble, mounted vertically, was inserted. The probe consisted of the viscometer head fitted with a standard MV II P profiled rotor of 36,8 mm diameter, rotating in a specially designed open-ended sleeve of 40,0 mm internal diameter that had 8 vertical slots cut into the wall. The size of the slots was such as to reduce the surface area of the sleeve by 25 per cent, and their purpose was to permit easier access of the mixture to the rotor. The equipment was calibrated by use of a standard oil and comparison of the results with those from the standard rotor–cup combination supplied by the manufacturer.

Model slurries were made by the mixing of silica flour (99,4 per cent purity, 150 mesh, average particle size 25 μm, comparable with that of mine wastes) containing 5 per cent by mass iron(III) oxide (A.R. grade, average particle size 0,5 μm) with distilled water to a total solids concentration of 70 per cent by mass. Wastes from Western Areas Gold Mine (WAGM) were mixed with distilled water to a consistency similar to that of the model slurry (71,4 per cent total solids by mass). In each test, the rotor speed was increased linearly with time up to a shear strain rate of $400\,s^{-1}$ in a time of 120 seconds, the shear rate being held constant for 6 seconds before the rotor speed was reduced to zero during the following 120 seconds. Plots of shear stress versus shear strain rate were recorded automatically.

Increasing amounts of either NaTPP (technical grade) or XP23/86 (a commercial slurry additive supplied by Silicate & Chemical Industries, Wadeville) were added to the slurries, and the tests were repeated until no further change was observed in the rheogram. All the tests were conducted at 20°C.

Results and Discussion

Rheograms of the silica–iron(III) oxide slurry with increasing amounts of additives are shown in Fig. 1, and similar rheograms for the mine wastes are given in Fig. 2. The unthinned suspensions of silica and iron(III) oxide exhibited typical pseudoplastic behaviour, whereas the addition of additive caused almost Newtonian response. The curves for the thick material tended to become parallel to those for the thinned slurries at higher shear rates. This suggests that the thick slurry could be modelled as a Bingham plastic by extrapolation of the linear part of each rheogram back to the shear-stress axis and definition of the intercept as a yield stress. The effect of the additive is thus to reduce the yield stress of the slurry rather than the viscosity (which corresponds to the slope of the rheogram). This reduction in yield stress in an actual pipeline considerably reduces the pumping power required to transport the material.

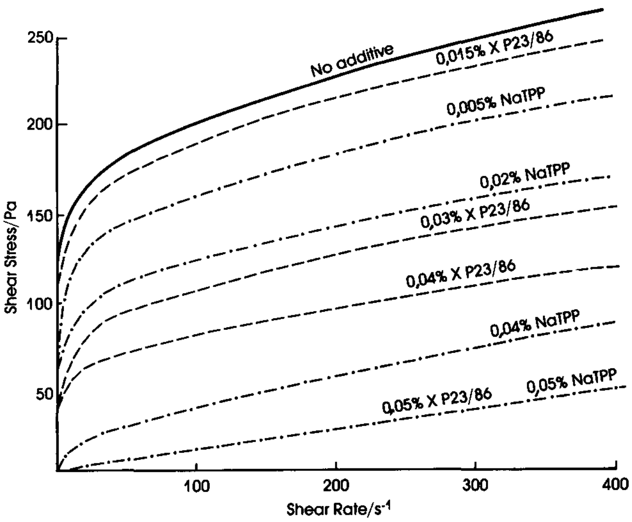

Fig. 1—Shear stress versus shear strain for an SiO_2–5% Fe_2O_3–H_2O suspension (———) at a total solids concentration of 70 per cent with increasing amounts of NaTPP (·—·—·) or XP23/86 (- - - -)

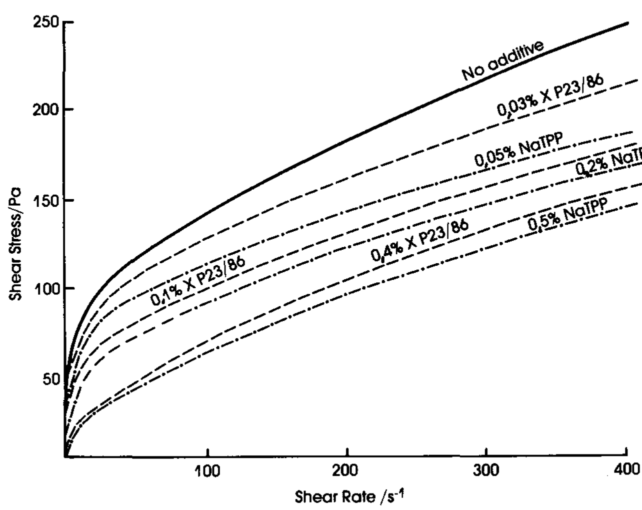

Fig. 2—Shear stress versus shear strain for WAGM tailings at a total solids concentration of 71,4 per cent with increasing amounts of NaTPP (·—·—·) or XP23/86 (- - - -)

Both additives produced similar overall effects in that the yield stress was reduced to zero, and the rheological behaviour of the slurry corresponded to that of a pure silica slurry at a solids concentration[8] of 70 per cent by mass. This implies that the iron(III) oxide, through interaction with silica and/or water, is responsible for the thickening of the slurry, and that the thinning effect of the polyphosphate indicates some interaction between it and the iron(III) oxide such as charged complex formation. The most likely factors influencing the thickening are

(i) binding of the water on the surface of the iron(III) oxide particles, effectively increasing the solids concentration, and
(ii) aggregation of the silica and iron(III) oxide particles, effectively increasing their resistance to flow.

Both these effects, involving relatively weak forces, could be overcome by mechanical stress, and hence flow would become easier at higher shear rates. Alternatively, binding could be displaced by stronger binding with polyphosphate, which could explain why the apparent viscosities (corresponding to the slope of the rheogram) of the thinned and unthinned slurries are parallel at high shear rates. The behaviour of the gold-mine waste was similar but, in this case, the slurry could not be thinned completely, that is, reduced to a Newtonian slurry. In a previous study on model slurry systems[8,9], the authors suggested that flow can be described in terms of two components: a Newtonian fluid flow and a 'solid' component, which occur consecutively so that the strain rates are added as

$$\frac{1}{\dot{\gamma}} = \frac{1}{\dot{\gamma}_N} + \frac{1}{\dot{\gamma}_S}, \qquad (1)$$

where $\dot{\gamma}$ is the shear strain rate, $\dot{\gamma}_N$ is the Newtonian flow, and $\dot{\gamma}_S$ is the solid flow. The term for solid flow arises as a consequence of particles having to shear past one another and, in doing so, to overcome an energy barrier that is a function of particle–particle interaction forces.

The solid-flow strain rate can be written in terms of the activation energy for flow ΔG as

$$\dot{\gamma}_S = A \exp(-\Delta G/RT), \qquad (2)$$

where R is the gas constant, T is the absolute temperature, and the constant A is characteristic of the physical nature of the suspended solid and can be expected to include such parameters as the particle-size and shape distributions. In turn, ΔG can be described in terms of ΔF, the energy required for particles to overcome interaction forces by thermal activation alone in the absence of an applied stress and $\hat{\tau}$, the 'flow stress barrier', which represents the height of the energy barrier in terms of stress; that is, at stresses above $\hat{\tau}$, only the Newtonian component of the shear strain rate will influence flow. The relationship between G and F is given by

$$\Delta F = \Delta G \left[1 - \left(\frac{\tau}{\hat{\tau}}\right)^p\right]^q, \qquad (3)$$

where p and q describe the shape of the energy barrier ($p = q = 1$, representing a cylindrical-shaped barrier). The value of constant A in equation (2) is unknown, and its value was assumed for the purposes of the present work. Calculated values of the material parameters ΔF and $\hat{\tau}$ presented below are thus relative, but do illustrate the chemical effects of the additives.

From rheograms such as Figs. 1 and 2, the slope of the curves at high shear rates was taken to represent the Newtonian component of viscosity. For particular shear stresses, equation (1) was used in the calculation of the solid shear strain rate from which values of ΔG can be calculated by use of equation (2). Values of ΔG for each rheogram were then plotted against the shear stress. It was found that values of $p = 0{,}75$ and $q = 1{,}5$ gave reasonably linear plots. Values of ΔF and $\hat{\tau}$ were then found from the intercepts of the curves with the ΔG and τ axes respectively.

The decrease in flow activation energy with increasing additive for each slurry is shown in Figs. 3 and 4. When additive was introduced into the model, slurry ΔF dropped fairly sharply after an initial lag period, whereas the mine waste showed a more gradual decrease. This can be interpreted as a sudden breaking-up of the structure in the model slurry, where iron(III) oxide is the only thickening agent, in contrast to the mine waste, where there are likely to be several agents causing aggregation, each of which will have different binding characteristics with the additive.

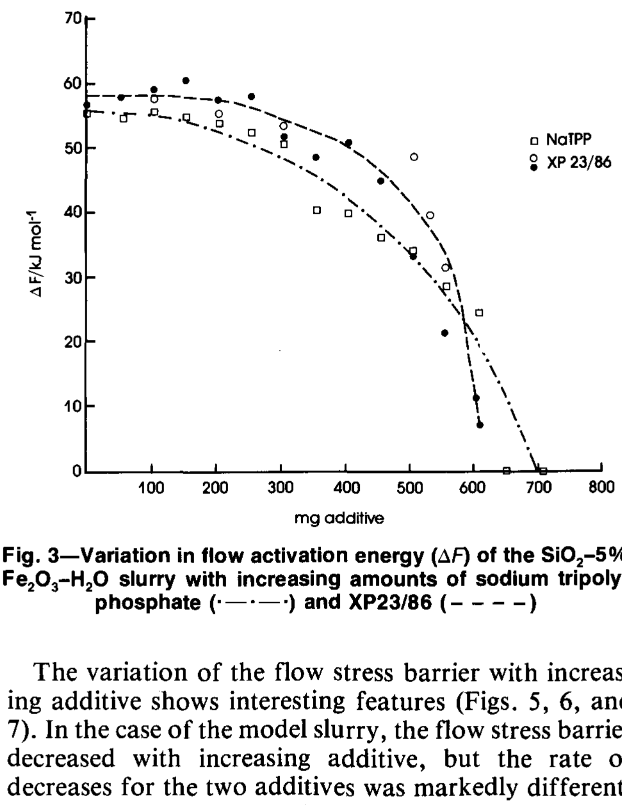

Fig. 3—Variation in flow activation energy (ΔF) of the SiO_2–5% Fe_2O_3–H_2O slurry with increasing amounts of sodium tripolyphosphate (·—·—·) and XP23/86 (- - - -)

The variation of the flow stress barrier with increasing additive shows interesting features (Figs. 5, 6, and 7). In the case of the model slurry, the flow stress barrier decreased with increasing additive, but the rate of decreases for the two additives was markedly different. With sodium tripolyphosphate, there was an initial drop followed by a flat portion and then another sharp drop. With XP23/86, there was an initial drop, a flat part, another drop, a second flat part, and a final drop. Although it may be coincidental, the titration curves of the two additives with acid show very similar patterns (Figs. 5 and 6). Thus, the flow stress barrier could reflect the thermodynamic binding of the iron(III) oxide with the respective additive; the formation of the different complex species would directly affect the size of the flow stress barrier.

The behaviour of the mine slurry was totally different. In the case of either additive, the flow stress barrier show-

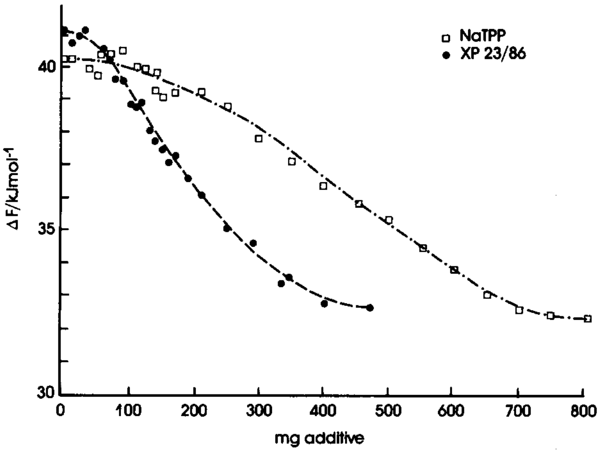

Fig. 4—Variation in flow activation energy (ΔF) of the WAGM slurry with increasing amounts of NaTPP (·—·—·) or XP23/86 (- - - -)

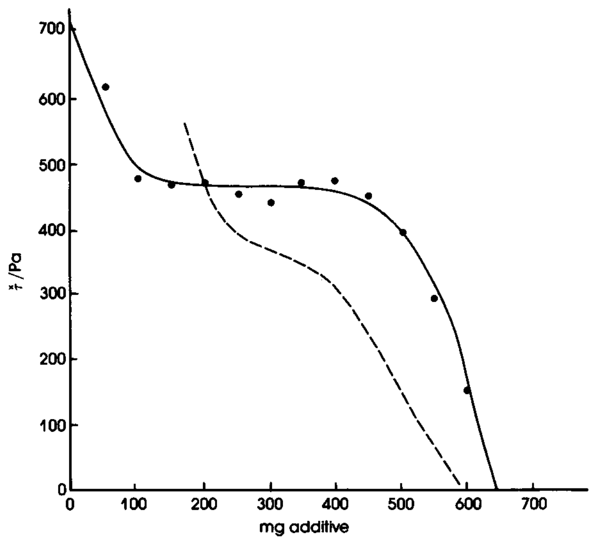

Fig. 5—Variation in flow stress barrier ($\bar{\tau}$) of the SiO_2–5% Fe_2O_3–H_2O slurry with increasing amounts of NaTPP (———) and the titration curve of NaTPP (- - - -)

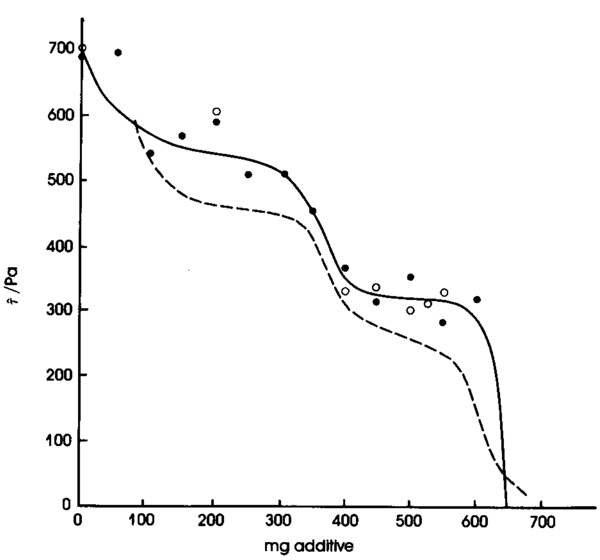

Fig. 6—Variation in flow stress barrier ($\bar{\tau}$) of the SiO_2–5% Fe_2O_3–H_2O slurry with increasing amounts of XP23/86 (———) and the titration curve of XP23/86 (- - - -)

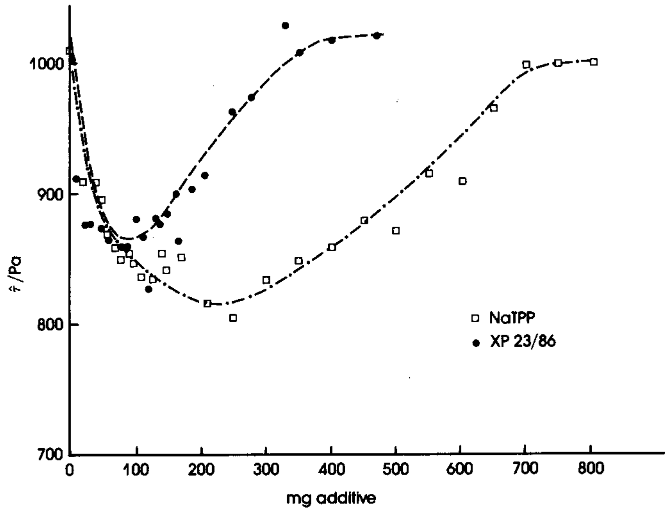

Fig. 7—Variation in flow stress barrier ($\bar{\tau}$) of the WAGM slurry with increasing amounts of NaTPP (·—·—·) or XP23/86 (- - - -)

ed a sharp initial drop followed by a rise back to the level of the original slurry. This effect was qualitatively similar for both additives, but was less pronounced and occurred more rapidly with XP23/86 than with NaTPP. A possible explanation of the difference between the mine waste and the model slurry could be the presence in the mine waste of compounds of alkaline earth metals such as calcium or magnesium, which are able after initial complex formation to form insoluble derivatives with the additives. This would effectively increase the solids concentration and, in doing so, increase the flow stress barrier. Mineralogical analysis indicated the presence of the clay minerals sericite and pyrophyllite, of which the latter contains magnesium. Elemental analysis also indicated the presence of magnesium. In preliminary laboratory experiments, a model slurry of silica and magnesium hydroxide carbonate had shown, on rheological analysis, behaviour very similar to that of the gold-mine waste, thus substantiating this hypothesis. More exhaustive studies are under way to confirm this aspect of the behaviour of silica slurry.

Conclusions

In silica-based industrial slurries, it is the presence of components such as iron(III) oxide that gives rise to adverse rheological properties, and these effects can be negated by the addition of dispersants such as sodium tripolyphosphate or other polyionic species that form charged complexes with iron(III) oxide. This behaviour can be illustrated by the quantitative analysis, in terms of flow activation energy and flow stress barriers, of mixtures of silica, iron(III) oxide, and water.

Typical gold-mine tailings showed similar qualitative behaviour but could not be thinned as effectively as the model slurry. This suggests the presence of additional thickening agents that do not form charged complexes with polyphosphate. Possible candidates include partially soluble alkali metal oxides, which would form insoluble precipitates, hence accounting for the re-establishment of the flow stress barrier.

By the use of the equipment and methods described, this behaviour can rapidly be assessed in the laboratory on relatively small quantities of material.

Acknowledgements

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Safer chemicals*

The use of chemicals at work has grown spectacularly over the past 15 years or so, but monitoring their possible dangerous effects on employees' health has hardly kept pace. Alongside the dangers of fire and explosion at the workplace, there lurk, unseen, insidious risks to the health of the growing army of workers who use or handle chemical substances in their daily tasks in advanced and developing countries.

Diseases caused by long-term exposure to low levels of toxic substances may not develop until years later. And occupational health specialists say some workers undoubtedly have become ill through contact with chemical substances not yet identified as hazardous. Virtually all processing and manufacturing industries nowadays are involved with harmful chemical substances, from the manufacture and use of adhesives, detergents, paints, and agricultural products to processes such as printing, electroplating, water treatment, and dry-cleaning.

The annual world production of chemicals is estimated at 400 Mt. Experts indicate that out of a total of 70 000 to 80 000 chemical substances on the world market, about 3500 to 8000 should be considered hazardous—and of those, 150 to 200 could be considered to cause cancer.

Occupational exposure limits for workers have been set for only a fraction of the chemical substances they may have to handle. An ILO publication lists some 1200 that have exposure limits adopted by various countries. While considerable advances have been made in testing new substances, the increasing cost and sophistication of the procedures are hampering progress.

Adequate statistics on occupational diseases and injuries resulting from exposure to chemicals are not available in many countries. This is due mainly to different criteria for recognizing, classifying, and reporting these ailments, which is further complicated by workers frequently changing jobs. In addition, gathering statistics on occupational diseases in developing countries is still in its infancy.

* Released by the International Labour Office, CH-1211 Geneva 22, Switzerland.

Since 1921 the ILO has adopted numerous labour conventions and recommendations dealing with safety in the use of specific chemical substances as their hazardous properties became known. But so far there is no comprehensive instrument on safety and health that would cover all types of chemicals at the workplace.

To close this gap in its legislative arsenal, the ILO put the issue of safety in the use of chemicals at work on the agenda of its International Labour Conference in June 1989, the objective being to draft an all-embracing convention and/or recommendation.

An ILO report that was prepared for the Conference says the proposed instruments should ensure a high degree of uniformity in the information given to enterprises and workers about hazardous properties of the chemicals they handle. Otherwise, in a world-wide industry with a migrant labour force there could be misunderstandings and possible fatal consequences.

Legislation on chemical safety is at present in an evolutionary phase in most countries and varies from one State to another, reflecting differing degrees of industrialization and work practices. The proposed ILO instrument would focus primarily on protecting the multitude of users of chemicals. Many of these are small enterprises whose employers and workers have no specialized knowledge of chemicals or their dangers.

Chemicals at the workplace should be classified according to the type and degree of hazards they involve. It is the responsibility of suppliers—whether manufacturers, importers, or distributors—to see to it that employers and workers are alerted to possible risks through accompanying labels and safety data sheets.

The instrument would also set standards for the safe storage, handling, and use of chemicals at the workplace, as well as their disposal. Safety training for workers and health surveillance are other potential elements.

Under the established ILO procedure, the process of formulating new safety and health standards for chemicals at the workplace will take two years, with the final text being approved at the 1990 annual Conference.

Air pollution

An international conference on air pollution is to be held in Pretoria from 24th to 26th October, 1990. The theme of the Conference is Air Pollution: Implications, Challenges, Options, and Solutions.

The ever-increasing pollution burden of the industrialized countries highlights the urgency to find a viable solution before irreversible damage is done to the environment and the life it sustains. Cognizance of the considerable experience that has been built up in the industrialized countries can be taken by the developing countries who appear to be approaching similar problems, albeit from a different perspective. Moreover, the industrial countries can glean considerable insight into their problems through exposure to the developing country's situations.

In common with other countries on the African continent, the population in South Africa is growing rapidly and is expected to double by the year 2020. Increasing pressure will be put on local natural resources, which in turn will lead to an increasing demand for electric-power generation, as well as the establishment of new secondary and tertiary industries. These developments will present new challenges for maintaining a well-balanced approach to ensure effective control of air pollution and hence provide adequate protection for the environment and its inhabitants.

This Conference will address the implications, challenges, options, and solutions for the 1990s that will have to be dealt with by policy-makers, industrialists, economists, environmentalists, and the broad scientific community. Delegates will discuss the requirements to project a well-managed environment into the 21st century.

The following topics will be discussed:

- Air quality and research
- Technology and research
- Environmental planning
- Community administration
- Public perceptions and aspirations
- Medical aspects
- Energy
- Impacts
- Legislation
- Indoor pollution.

The Conference will be of interest to

- Environmentalists and environmental engineers
- Community administrations/local authorities
- Research organizations
- Universities and technikons
- Ventilation engineers
- Industries, especially those concerned with pollution
- Industrial management
- Industrial hygienists.

Papers are called for on the above or related topics:

- *Formal papers*: for oral presentation; 12 pages in length; to be included in the volume of proceedings.
- *Poster papers*: for graphic presentation *and* a brief (three-minute) verbal presentation during a special session at the Conference; short papers to be included in the proceedings.

Prospective authors (for both formal or poster papers) should submit a 500-word extended abstract/summary to the Conference Co-ordinators not later than *31st July, 1989*. Authors will be informed of the acceptance of their papers by November 1989. Complete papers must reach the Co-ordinators by 28th February, 1990.

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