



Selective leaching of phases occurring in charge chrome

by A. Wedepohl* and P. Ellis*

SYNOPSIS

Selective leaching of phases in charge chrome is used in a variety of industrial processes for the production of chromium chemicals. A mineralogical study was made of a range of local charge chrome samples, at various stages of leaching in sulphuric acid (20g/l at 90°C), using mainly a scanning electron microscope (SEM) together with an energy-dispersive spectroscopy analyzer (EDS), and X-ray diffraction techniques.

It was found that the leaching behaviour of the different types of charge chrome depends largely on the nature of the secondary phases, which in turn depends upon whether the silicon content is above or below 4 per cent by mass. The leaching behaviour of high-chromium ferrite is anomalous, and it is postulated that the process is analogous to the corrosion of brass by dezincification.

Keywords: charge chrome leaching, scanning electron microscope

Introduction

It is generally accepted that exporting value-added products, rather than raw materials, benefits the South African economy. This applies particularly to the metallurgical industry. With this in mind, Mintek has been exploring methods of facilitating the production of chromium chemicals. A potential starting material is ferrochromium. It would be of particular benefit if a use were found for the ferrochromium fines that are generated during the handling of charge chrome. With this in mind, the selective leaching of phases in a series of local charge chrome samples, having different silicon contents, was studied. According to the specification, charge chrome has a chromium content of 52-58 per cent by mass and a carbon content of 6-8 per cent¹. The samples chosen for investigation had carbon and silicon values of 6-7 per cent and 1.3-8.2 per cent respectively (Table 1). Chromium, iron and silicon were analysed by wet chemistry, and carbon was determined by the Leco method.

Note that the very high-silicon sample is abnormal, and was produced during a non-ideal run in an experimental plasma furnace. It was investigated out of curiosity, rather than

with a view to the practical use of such an alloy.

Experimental methods

Initially, bulk samples were characterized using an ARL electron microprobe (wavelength dispersive spectroscopy) and X-ray diffraction. The information gained was an essential part of the investigation. However, it was realized that it was necessary to study individual phases to clarify the leaching processes taking place, and that the good imaging capability of a scanning electron microscope (SEM), together with an energy-dispersive spectroscopy analyser (EDS) would be ideal for further investigation. A Hitachi S-450 SEM, together with a PGT EDS analyser, was therefore used, and the following method was developed to carry out interrupted leaching studies of individual particles. After the samples had been milled to <53µm, polished sections were made. Initial selection and analysis of three multi-phase particles from individual polished sections of each type of ferrochromium were carried out, and backscatter electron photomicrographs taken. The polished sections were then subjected to attack by H₂SO₄ (20g/l at 90°C). These conditions mirrored those found to give the best balance between efficiency and cost-effectiveness in the pilot plant project, which was running concurrently at Mintek, to produce chromic hydroxide from charge chrome by low-acid leaching of milled samples². Extra ferrochromium fines were always present in the leaching vessel to ensure reducing conditions. After each leaching period, the phases present in the selected particles were again analysed, and photographed by means of backscatter electrons. Four hours was chosen as the maximum time to subject the polished sections

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Table I

Type and composition (% by mass) of ferrochromium samples investigated

Sample	Cr	Fe	C	Si	Total
Low-Si	56.8	35.1	6.5	1.13	99.53
Granulated	52.7	36.6	6.7	3.32	99.32
Average-Si	53.2	36.1	6.5	3.53	99.33
High-Si	52.2	35.1	6.4	5.59	99.29
Fines	50.5	34.5	6.25	5.96	97.21
Very high-Si	50.4	33.7	5.63	8.26	97.99

to acid attack, since in the pilot plant tests it was found that negligible additional chromic hydroxide was produced by leaching the fines for more than four hours.

Characterization

X-ray diffraction patterns of the milled samples were obtained using a chromium x-ray tube ($\lambda=2.2897\text{\AA}$) and also by means of a molybdenum x-ray tube ($\lambda=0.7093\text{\AA}$). The long wavelength of the former spread out the overlapping peaks in the d-value range of 2.04 to 1.99 \AA , making it easier to resolve them. The shorter wavelength of the molybdenum tube compressed the patterns so that diagnostic peaks with lower d-values could be recorded at reasonable angles (2 to 55°). It was found that the major phase present in all the samples was carbide of the type $(\text{Cr,Fe})_7\text{C}_3$. The second most abundant phases depended on the silicon content. In the low- to medium-silicon samples (1.3-4 per cent), this phase was ferrite, i.e. α -Fe,Cr solid solution which can dissolve up to 14 per cent silicon by mass. There were two population groups of this phase, low-chromium and high-chromium ferrite (Table II). The ferrite was identified using diagnostic peaks in the low d-value range of the diffraction pattern, i.e. 1.013, 0.906 and 0.828 \AA (JCPDS pattern 6-0696). It was not possible to separate the two groups by XRD. However, once the phase had been identified by this method, it was

discovered by means of EDS analysis that both low-chromium and high-chromium ferrite were present. The predominant secondary phase in the granulated ferrochromium was the high-chromium variety. In high-silicon samples (4.5-8.2 per cent), ferrite was replaced by the silicide $(\text{Fe,Cr})_3\text{Si}$ containing stoichiometric amounts of silicon (14.4 per cent) and another high-silicon phase containing approximately equal amounts of iron and chromium and about 12 per cent silicon. This was found to be the t.c.p. σ -phase, which is known to cause brittle fracture in high-chromium steels⁵. These two phases were also conclusively identified from x-ray diffraction patterns using the diagnostic peaks in the low d-value range, i.e. 1.413, 1.154 and 0.999 \AA for the silicide (JCPDS pattern 45-1207) and the envelope of lines between 0.83 and 0.78 \AA for the σ -phase (JCPDS pattern 5-0708). The lines for the silicide and the σ -phase do not overlap with each other or with lines from the ferrite or carbide patterns. In addition, it was possible to separate the 1.999 \AA line of the silicide pattern from the 2.04 and 2.02 \AA lines of the carbide pattern, using the chromium tube.

Figure 1 shows photomicrographs of particles typical of the two broad groups of charge chrome. As can be seen, not only does the σ -phase show brittle fracture, but so does the silicide. This would explain the lower than normal chromium content of ferrochromium fines, and the higher than average

Table II

EDS analysis of phases in charge chrome (% by mass)

Phase	Cr	Fe	C	Si
$(\text{Cr,Fe})_7\text{C}_3$	68.5	22.1	8.9	0.5
High-Cr ferrite	23.3	64.7	-	11.9
Low-Cr ferrite	12.6	75.4	-	12.0
$(\text{Fe,Cr})_3\text{Si}$	8.3	74.1	-	17.5
σ -phase	40.1	46.2	-	13.7

Notes:

- EDS analyses in Tables II-IV are all standardless analyses and are normalized.
- Carbon could not be analysed by means of the EDS. In the case of the carbide it was calculated by stoichiometry. Ferrite can dissolve very little carbon.
- Silicon values are known to be high when analysed by this method, possibly due to the excitation of silicon in the silicon detector and errors in the ZAF correction for standardless analysis. $(\text{Cr,Fe})_7\text{C}_3$ should not contain any silicon, and the EDS analyses of the other four phases shown in the table gave silicon values of about 2 per cent higher than electron microprobe analyses of the same phases.

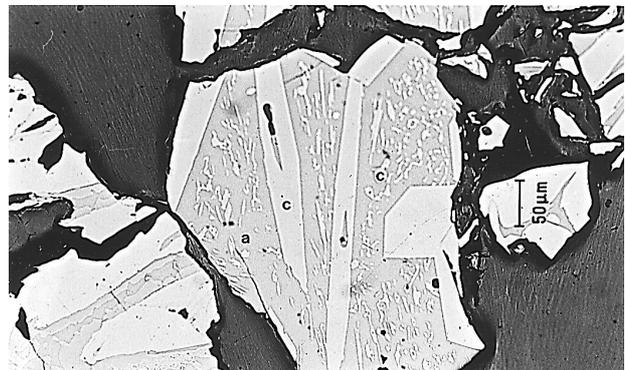


Figure 1(a)—Photomicrograph of a particle from charge chrome fines, consisting of carbide crystals set in a matrix of eutectic low-carbon ferrite (a) and $(\text{Cr,Fe})_7\text{C}_3$ carbide (c)

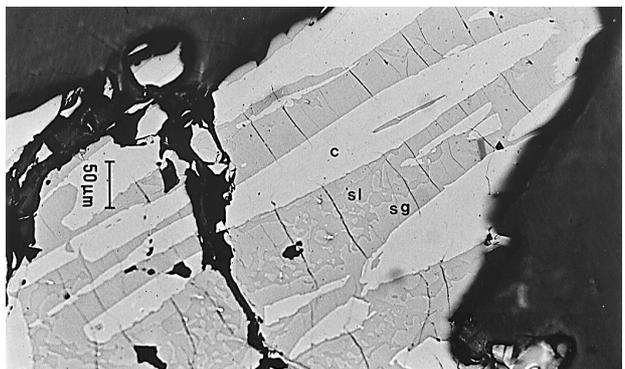


Figure 1(b)—Photomicrograph of a particle from high-silicon charge chrome, consisting of $(\text{Cr,Fe})_7\text{C}_3$ carbide crystals (c) set in a matrix of $(\text{Fe,Cr})_3\text{Si}$ silicide (sl) and σ -phase (sg)

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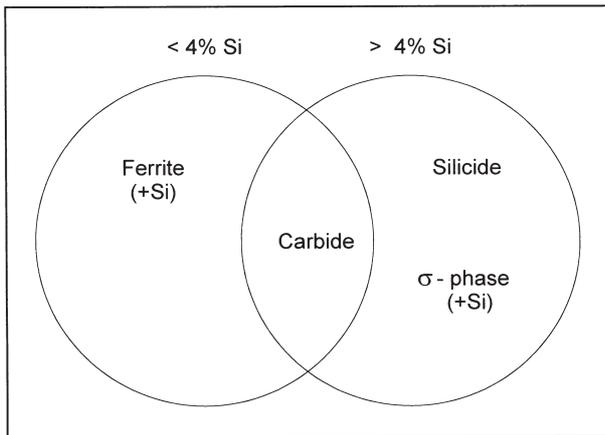


Figure 2—Digrammatic representation of the phase composition of the two broad groups of charge chrome

silicon content, since due to the brittle nature of these phases, they would be over-represented in the fines. Table II shows average EDS analyses of the phases mentioned above, and Figure 2 summarizes the phase composition of the two groups of charge chrome.

Minor phases occurring in all the samples were small, hard (about $2\mu\text{m}$), square or dendritic crystals of titanium carbonitride, which appear pink under the optical microscope, and the occasional inclusion of titanium sulphide. In addition, in the very high-silicon charge chrome, a second silicide, $(\text{Fe,Cr})_2\text{Si}$ occurred in small quantities.

Leaching behaviour

Leaching times chosen for the investigation were 30 minutes and 4 hours. It was found that after 4 hours a large percentage of the carbide phase had dissolved in all the samples. Where the major secondary phases were ferrite, i.e. in the low- and medium-silicon samples, some particles of low-chromium ferrite appeared to dissolve at a slower rate than the carbide (Figure 3), while the high-chromium ferrite initially dissolved faster than the carbide and had a pock-marked appearance (Figure 4c). However, after the first 30 minutes, the latter particles appeared to have become passivated, and the rate of carbide dissolution overtook that of the ferrite (Figure 4d). Where the major secondary phase was silicide i.e. in the high-silicon samples, the silicide phase showed no sign of dissolution, and appeared to have a high resistance to acid attack (Figure 5.). In the latter samples, it was also observed that all the σ -phase was almost totally dissolved within 30 minutes. A summary of the leaching behaviour of the five most important phases is shown in Figure 6.

The composition of the carbide, low-chromium ferrite, and silicide crystals remained essentially the same at the different stages of leaching. However that of high-chromium ferrite changed, showing a decrease in chromium content and a slight increase in silicon. This effect is shown in Table III.

De-alloying

We suggest that for high-chromium ferrite, the leaching process is analogous to the dezincification of brass. In this latter process, pitting corrosion of yellow brass (Cu 65%, Zn

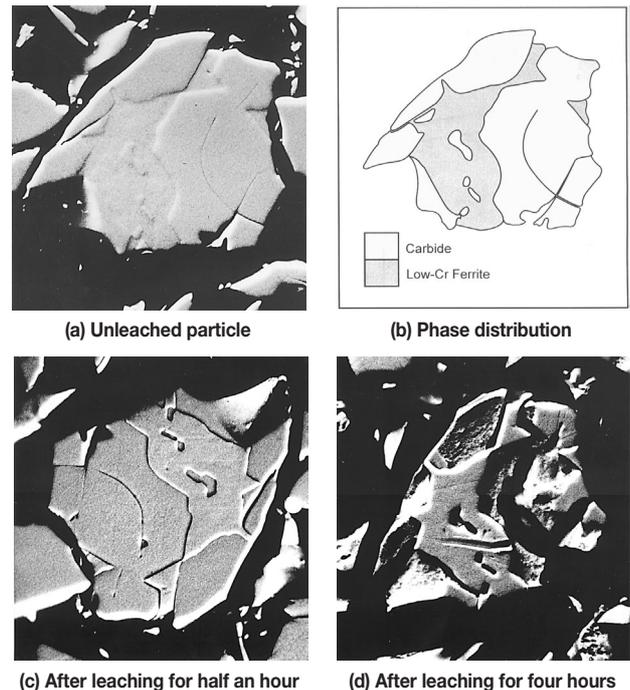


Figure 3—Leaching sequence of low-chromium ferrite/carbide particle from average silicon charge chrome (backscatter electron SEM photomicrograph)

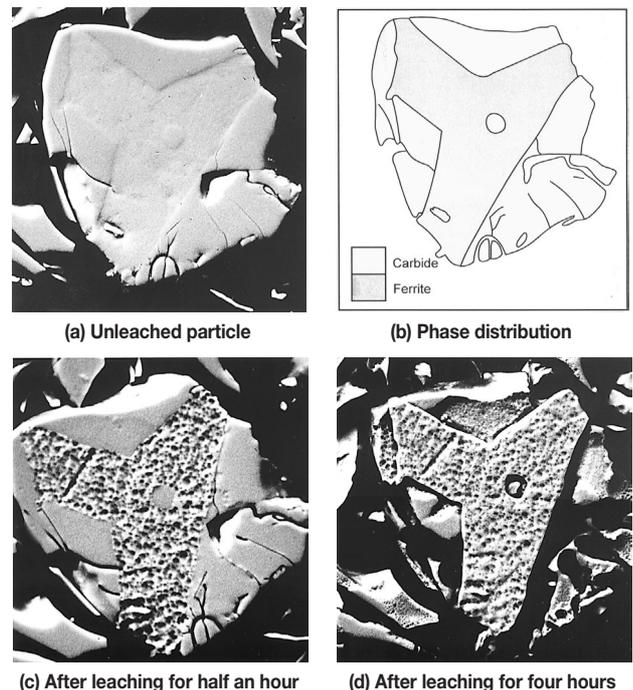


Figure 4—Leaching sequence of high-chromium ferrite/carbide particle from average silicon charge chrome (backscatter electron SEM photomicrograph)

35%) in acid is caused by dissolution of brass with subsequent re-deposition of pure copper on the corroded surface. Pure copper is relatively resistant to acid attack⁴. The equivalent process for high-chromium ferrite containing large amounts of silicon in solid solution would be that the surface layer of a ferrite particle is rapidly dissolved in sulphuric acid. All the elements except for a few per cent of the chromium, which stays in solution, are then redeposited on the surface

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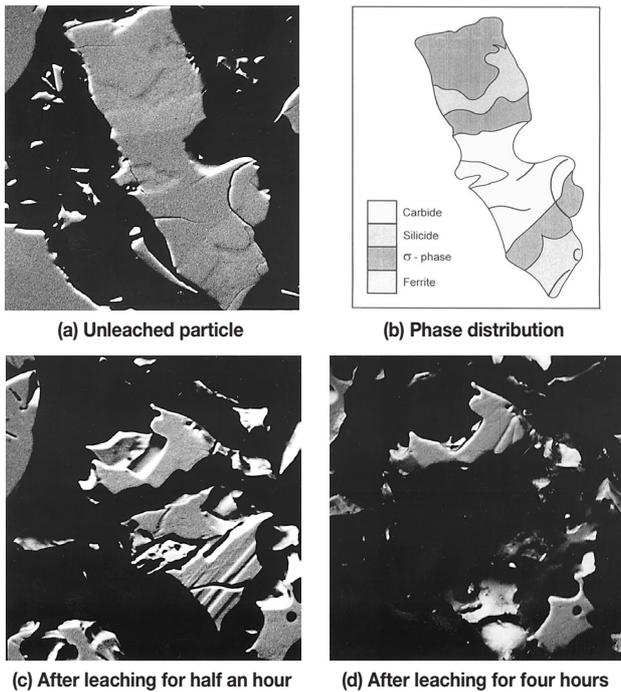


Figure 5—Leaching sequence of silicide/ σ -phase/carbide particle from high silicon charge chrome (backscatter electron SEM photomicrograph)

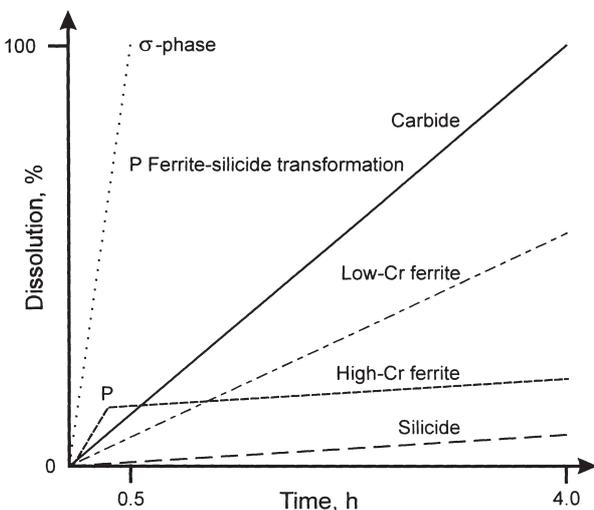


Figure 6—Relative leaching rates of the main phases in charge chrome

Table III

Mean EDS analysis of high-chromium ferrite in particles of granulated charge chrome at different stages of leaching, % by mass

Leaching stage	Cr	Fe	Si
Unleached	23.3	64.7	11.9
30 Minutes	17.1	68.9	14.0
4 Hours	13.5	70.9	15.6

of the source particle as silicide, which is resistant to acid attack. The removal of a few per cent of chromium would push up the silicon proportion of the redeposited phase sufficiently to give it a composition equivalent to $(\text{Fe,Cr})_3\text{Si}$. The crystal structures of ferrite and this silicide are similar in that they are both cubic. However, ferrite is body-centred cubic whereas the silicide is face-centred cubic, and according to the information given with the JCPDS patterns for the pure phases, the unit cell of the silicide has linear dimensions which are almost exactly double those of the ferrite ($a_{\text{ferrite}}=2.8664\text{\AA}$ whereas $a_{\text{silicide}}=5.6533\text{\AA}$). X-ray diffraction patterns showed them to be two distinct phases and not part of the same solid solution series. Dissolution of the ferrite beneath the passive silicide layer can still take place, since the latter is porous.

The above hypothesis is supported by the fact that XRD patterns of all bulk residues, whether the starting material had been low-, medium-, or high-silicon ferrochromium, showed the residues to consist primarily of the silicide, $(\text{Fe,Cr})_3\text{Si}$, with minor amounts of the carbide, $(\text{Cr,Fe})_7\text{C}_3$.

Figure 7 shows the relative heights of the XRD peaks at each stage of leaching.

The EDS analyses of the surface of high-chromium ferrite particles at each stage also supports the hypothesis, as do the analyses of random particles in a residue of mixed fines, that had been leached until no further reaction took place. The latter all had the composition of the silicide (Table IV).

Formation of silica gel

It was observed that clouds of silica gel surrounded residual

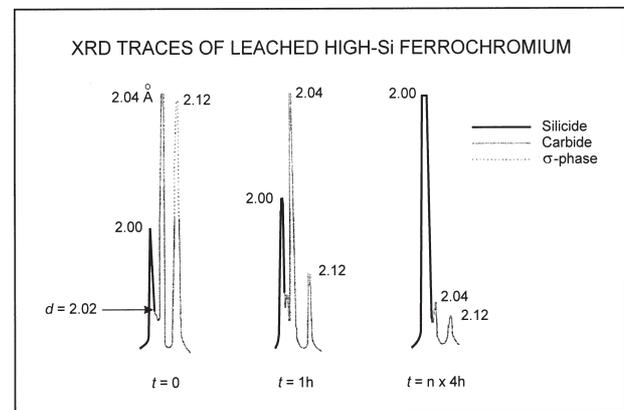


Figure 7—XRD traces of leached bulk samples of high silicon charge chrome

Table IV

EDS analysis of random particles in the residue of mixed fines, which had been leached until no further reaction took place, % by mass

Particle	Cr	Fe	Si
1	7.8	75.6	16.6
2	8.9	75.8	15.3
3	9.1	72.7	18.2
4	7.3	75.4	17.3
Mean	8.3	74.9	16.8

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particles after milled charge chrome had been leached for more than 4 hours. This arises from the leaching of silicon to form $\text{Si}(\text{OH})_4$, which subsequently forms silica gel⁵, $(\text{SiO}_2)_n$. The origin of the silicon is not the occasional particle of quartz, which was observed as a contaminant in some samples, because they appeared to be completely unaffected by the leaching process. Among the metallic phases containing significant amounts of silicon, the σ -phase is the one that dissolves most readily and probably contributes most to the silicon content of the leach liquor.

Choice of charge chrome for different applications

The silicon content of charge chrome plays a major role in its leaching behaviour. In particular, if it is intended to leach the ferrochromium for the recovery of chromium, then the low-to average-silicon variety would be more suitable, since the deposition of colloidal SiO_2 , ostensibly resulting primarily from the dissolution of σ -phase in high-silicon charge

chrome, could cause problems in leaching vessels and pipelines

Acknowledgements

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Engineering team of the future*

At a SAIMM workshop attended by practicing engineers, trainers, and educators, the perspective of the engineers within the minerals and metals sector was discussed.

One of the objectives of the workshop was to identify the real needs of industry in terms of the number of members of the engineering team and the skills required by these members. The focus was on members of the 'professional' engineers in the areas of Mining, Extraction Metallurgy and Materials Engineering. An attempt was made to highlight, for the benefit of employers, engineering employees and the youth, a realistic view of the 'Engineering team of the future'.

A preparatory stage was to undertake a structured interview with a representative sample of visionaries within the mining and metals industry. The visionaries were unable to determine numbers of engineers for their sector but gave very valuable insight into the nature of the engineering profession of the future. Particularly highlighted by the visionaries were the following areas:

Business factors including industry

Globalization and international competition require that the members of the engineering team are able to effectively access and utilize the latest technology. Engineering team members will have to apply a holistic business approach to all the production activities. The role of the Mega Company is rapidly changing to focus activity on outsourcing of specialist and even core business activities. Close to the work front there is a move to multiskilling cost containment through multiskilling of the work force to ensure maximum plant utilization, which is seen as a significant cost factor. Innovative technology is likely to develop through research partnerships internationally rather than internally. Tightening legislative policies is likely to inhibit industry expansion within South Africa.

Factors influencing education and training

The MQA and more general SAQA policies will impact greatly on requirements from tertiary education and career-based education entities.

Funding to educators and student support is likely to decrease with consequent challenges to both. The mineral and metals industry and engineering in general does not enjoy the positive image of other professions. The foundation of mathematics and science from the school system is seen as a long-term problem. Life-long learning and professional development is seen as vital to maintaining a competitive edge.

Outcomes from the collaborative workshop

Recruitment and selection

It is known that the industry is shrinking, but it can only survive if the quality of new entrants matches the challenges of the future industry.

- a) The minerals and metals industry must be marketed to the public and in schools particularly—SAIMM can play a significant role.
- b) Bursaries must be available and advertised for both technikons and universities.
- c) Improved of mathematics, science and technology teaching at schools. The SAIMM in collaboration with other SET NGOs can influence the government funding formula by high level representation. Further contributions can be made by SAIMM's organization of teacher/trainer visits to mines and metallurgical plants.

Further and higher education

The education for young engineers in mining, metallurgy and materials technology must be appropriate. The roles of technikons and universities in serving industry needs must be detailed. Whilst the MQA is likely to provide major input in the required outcomes, teaching capacity must be ensured by suitable industry investment.

- a) *Market Research to establish numbers and skills*—is a market research project justified? The SAIMM can continue to carry out surveys of current and future requirements through using its council members to source information from companies. This information can be fed to tertiary institutions, the MQA and back to industrial companies, so that maximum utilization of education resources can be obtained and realistic planning done.
- b) *Clarify funding of tertiary education*: The value of discipline specific education must be matched by injection of finance. Education and training is costly but vital for the long-term health of the industry. The rule should be that user pays. i.e. where courses are non-viable due to numbers or facility requirements the user should support these courses to break even. The SAIMM could be involved in lobbying industry to support courses that are needed but are non-viable.
- c) *Provide vacation and experiential training opportunity*: Where experiential training semesters or vacation work is required for a particular course of study. The SAIMM can conduct a survey of

Engineering team of the future* (continued)

mines prepared to accommodate private students for experiential training/vacation work. The SAIMM could become a broker for experiential training opportunity and vacation work.

- d) *Design curricula according to industry needs:* Providers of education need to focus on the education content required by the users—this will ensure that qualifications have intrinsic benefit for the user. The MQA is likely to identify all directly applicable, ‘useful outcomes’ and to register these with SAQA; MQA will see to it that these outcomes are included in curricular of providers of education and training. The providers must also input the broader educational aspect that will give body to the qualification. The SAIMM can become involved with the MQA and eventually register as ‘Quality assurers’ for the MQA. Further, the SAIMM can identify suitable members to act on SAIMM’s behalf as members of accreditation teams.

Socialization and initial training

It was established that the rate of change in the economic, political and social areas both in the minerals and metals industry as well as the country as a whole, has had a negative impact on the success expected when bringing young engineers into the industry. Many of the new breed of engineers cannot adjust to the responsibilities or expectations of the business environment. Cultural conflict is also possible.

- a) *Dealing with change:* The understanding of the cultures of all parties must be promoted actively. The changes that must be handled include: cultural/racial, economic/business, academic to real world. The SAIMM can be an agent to expose these problems and possible solutions through colloquia.
- b) *Break down cultural barriers:* Until a sufficient number of non-white persons are in senior positions there will always be some element of cultural barrier. Perhaps the barriers must be broken by promoting understanding of the cultures of the great range of persons in our industry. The SAIMM can be instrumental in bringing persons together at workshops to hear of cultural norms that are different to their own. Young engineers are unlikely to realize their full potential until they can work together with persons of other cultural backgrounds.
- c) *Improve induction training and mentorship:* It is believed that many young engineers do not realize their potential due to inappropriate induction programmes and lack of mentorship. Particularly with university graduates the induction period is in extreme contrast to their university life and their expectations. These initial impressions of the industry result in large numbers of graduates leaving the industry at the earliest possible opportunities. Induction programmes could be improved so that the young engineer is given responsibility and gains a feeling of worth during the first four years of employment. The SAIMM could conduct interviews of young engineers and publish the results, so as to highlight the shortcomings in induction programmes. HR managers can also give useful insight into the reasons young engineers leave their sponsors or first employment. The early years of development of a young engineer is often the most critical. It is believed that all successful members of the engineering team have had a supporting mentor in their early years as young engineers. It is believed that every successful member of the engineering team has a responsibility to mentor one or more young persons entering the team. The SAIMM can champion this cause by being an example to other professional bodies. The SAIMM could encourage its members to identify one or more persons for whom they could be the mentors.

Development and retention

Despite the current climate in the mining industry it is believed that retaining skills has significant advantages for a company. It is felt that many young and not so young engineers are incorrectly deployed into areas that do not suit their personality or interests.

Successful members of the engineering team are invariably those that have found the right niche for themselves—often by coincidence. An effort needs to be made to locate individuals into positions where ‘work is their hobby’. Many of the problems of salary, perks, etc. become less important if the job is interesting and suits the individual.

- a) *Change the employment model to meet changing industry requirements:* Just as it is important to fit the right person to a job it is recognized that the employment model is undergoing overhaul. Out-sourcing is resulting in opportunities for specialist self-employment in a wide variety of engineering fields. Within companies there is a tendency to dispense with ‘head office consultants’ in favour of decentralized profit entities/business units. Many young engineers are placed in management positions resulting in loss of technical expertise and mismatched personality/job. The SAIMM could conduct a survey and publish the results that indicate the degree of suitability of young engineers in their current jobs.
- b) *Performance-based remuneration:* The systems of fixed salaries are being replaced by performance-based remuneration. The SAIMM could conduct a survey that identifies the relative remuneration that is performance based.
- c) *Strategy for maximizing career paths:* Young engineers must know that there is a planned career path for them. Without this motivation retention is not likely to be successful within a large company. The SAIMM could conduct a survey that identifies the relative satisfaction of the path of a young engineer’s career.

Continuing education and training

The base qualification becomes only a pleasant memory within a few years of qualifying. The really useful learning comes about by job experience and focus areas relevant to the specific discipline. The life-long learning activity is vital for young and old engineers alike.

- a) *Develop top technical specialists:* SA cannot only rely on the developed world for solutions to local technical problems. It is believed that relatively few top specialists are required locally, but it is incumbent on individuals and companies to identify specialist requirements and thereafter invest in these individuals to serve the local market. Young engineering academics must be matured to serve the industry. SAIMM cannot make any meaningful contribution in this regard.
- b) *Inculcate business and entrepreneurial skills and ethics:* The mega company ethos is disintegrating and opportunities exist for young engineers to run their own business/small mines, etc. Even within the remaining large companies the business ethic is becoming more and more important. Whilst the SAIMM’s contribution might be limited in this regard it would be possible for SAIMM to run colloquia that promote small business activities for young engineers. Role models could be highlighted in the *Journal* and more generally published. The SAIMM could also act as a broking agency for small projects and research activities.
- c) *Promote personal responsibilities for on-going development:* Through its membership of young engineers the SAIMM can make available professional development opportunities that include technical sessions provided by the SAIMM.
- d) *Promote professional registration:* The value of registration within the minerals and metals industry has been much debated. With the new dispensation in South Africa, professional registration will become a pre-requisite for many of the senior positions and within private small companies. The SAIMM can promote the registration philosophy by instituting discount fees for registered members, or lower colloquia fees, etc. ♦

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