Technical Note: Solubility of nitrogen in experimental low-nickel austenitic stainless steels

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Synopsis

*The amount of nitrogen contained in an austenitic stainless steel affects its properties significantly. The maximum content of nitrogen feasible in a range of experimental low-nickel austenitic stainless steels containing significant additions of copper is evaluated. The nitrogen content is calculated based on published interaction coefficients, and by use of the F*A*C*T thermodynamic computer program and database. The differences between the two methods of prediction can be attributed to inaccuracies in the published interaction coefficients. The calculated nitrogen contents of some experimental alloys are compared with the actual nitrogen contents obtained when the alloys were produced in an induction furnace. The actual nitrogen contents obtained were higher than those predicted by either method, and this is believed to be due to a supersaturation of nitrogen occurring in the melt, which was not relieved during the short period in which the charge was molten. It*

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Introduction

The addition of nitrogen to stainless steels can have substantial effects on their mechanical and corrosion properties. Nitrogen is a strong austenite-forming and stabilizing element, and is a strong solid-solution strengthener. It is also known to significantly improve resistance to corrosion. Austenitic stainless steels with high nitrogen contents possess an increased tensile strength, without a reduction in ductility or fracture toughness[1-7]. Currently, the commercial alloys with the highest nitrogen content are based on Fe–18%Cr–1 to 7%Ni–1 to 18% Mn, and these alloys can contain up to 0,6 per cent nitrogen. The grades XM-17, 18, 19, 29, and 31 in ASTM A240, and DIN 1.3816 (which is used for generator end rings) are examples of such alloys. However, experimental or semi-commercial alloys containing up to 1 per cent nitrogen are also known[1-5,7,8].

A number of factors influence the solubility of nitrogen in iron alloys, namely alloy composition, crystal structure, temperature, and the pressure of gaseous nitrogen in the atmosphere above the alloy. Additions of chromium, manganese, and molybdenum to liquid steel increase the nitrogen solubility, while additions of nickel, carbon, silicon, and copper decrease it[9-12]. Although the present work examines the solubility of nitrogen in only the liquid phase, it is also a requirement for the commercial application of such alloys that their nitrogen content is retained in solution during solidification and in the solid phase. Porosity induced by nitrogen coming out of solution during solidification is an important factor limiting the more widespread adoption of high-nitrogen alloys[13]. Direct solidification into the austenite phase field is very desirable[13] because the solubility of nitrogen in ferrite is much lower than in austenite. This requirement presents a problem in the 300-series stainless steels (which contain some δ-ferrite at elevated temperatures), but is possible in selected compositions such as Fe–15%Cr–15%Mn alloy with sufficient nitrogen in solution[14].

Cortie[15] *et al.* have described a series of low-nickel austenitic stainless steels that contain up to 3 per cent copper and varying amounts of nitrogen. These materials were developed in a collaborative research effort by Mintek, Samancor's Manganese Division, and R.A. Lula Consulting (USA) in a programme to find soft and formable austenitic stainless steels that contain less than 4 per cent nickel. The copper addition is required in order to raise the stacking-fault energy of the alloys, which is essential to ensure a soft material with good formability. These materials contain additions of nitrogen in order to assist in the formation and stabilization of the austenite phase. It was necessary to determine the maximum solubility of nitrogen in the melts of such alloys, and the extent to which it is decreased by copper. A subset of the range of possible alloys, in this case containing a carbon addition of 0,1 per cent, was chosen for the present investigation. The particular alloys were designed to be substantially austenitic, even during cold working. Other alloys developed in the collaborative investigation mentioned[15] have lower carbon contents. The results of the present investigation may also be of more general interest, since two methods for predicting the nitrogen content of a liquid steel are compared and checked against experimental data obtained from melts made in an induction furnace. In the first method, the solubility is calculated from the published thermodynamic interaction coefficients and, in the second, use is made of the Facility for Analysis of Chemical Thermodynamics, F*A*C*T, which is available from McGill University in Montreal, Canada, to on-line subscribers.

was evident that the experimental alloys can contain between 0,25 and 0,40 per cent nitrogen (depending on temperature, composition, and nitrogen pressure) when melted in a sealed induction furnace, and this is more than adequate for the purpose of forming and stabilizing the austenite phase.

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References

1. Reed, R.P. Nitrogen in austenitic stainless steels. *J. Met.*, Mar. 1989. pp. 16–21.
2. Speidel, M.O. High nitrogen stainless steels: austenitic, duplex and martensitic. *Stainless Steels '87*. London, The Institute of Metals, 1988. pp. 247–252.
3. Speidel, M.O. Corrosion science of stainless steels. *Stainless Steels '91*. Tokyo, The Iron and Steel Institute of Japan, 1991. pp. 25–35.
4. Speidel, M.O. High manganese, high nitrogen austenitic stainless steels: their strength and toughness. *High manganese austenitic stainless steels*. Lula, R.A. (ed.). ASM, 1993. pp. 135–142.
5. Rawers, J., Asai, G., Doan, R., and Dunning, J. Mechanical and microstructural properties of nitrogen-high pressure melted Fe–Cr–Ni alloys. *J. Mater. Res.*, vol. 7, no. 5. 1992. pp. 1083–1092.
6. Cortie, M.B., Missio, L., Biggs, T., and Shaw, M. The effect of nitrogen additions on a metastable 17% Cr austenitic alloy containing Mn, Ni and Cu. *High manganese austenitic stainless steels*. Lula, R.A. (ed.). ASM, 1993. pp. 199–207.

Experimental

Nitrogen Solubility Based on Published Interaction Coefficients

Sievert's Law has been found to hold under equilibrium conditions for nitrogen pressures of up to 200 MPa and chromium contents of up to 50 per cent [5,9-12], and the calculation here of the solubility of nitrogen has been based on that assumption. The method used is standard and is described in various texts[16,17], as well as in a previous article in this *Journal* by Turan and Koursaris[18].

The interaction coefficients used are given in Table I. The values of these coefficients are given in the literature[9,12,17,19], but there is considerable scatter between the coefficients reported, and the most reliable values appear to be those reported in the Steelmaking Data Sourcebook[17]. Accordingly, these are the values that were used in the present calculations.

The units of T in the expressions in Table I must be kelvin. Where the value is given at a fixed temperature, the *Data Sourcebook* advises that a linear extrapolation of the form

$$e_i^j(T) \approx \frac{T'}{T}.e_i^j(T')$$

can be used provided that the difference between T and T' is not too large.

Table I

Interaction coefficients for alloying elements

Interaction coefficient	Value
e_N^C	0,130 at 1873 K
e_N^{Cr}	$-148/T + 0,033$
$r_N^{Cr,Cr}$	$1,56/T - 0,00053$
e_N^{Cu}	0,009 at 1873 K
e_N^{Ni}	0,007
e_N^{Si}	0,048
e_N^{N}	0
e_N^{V}	$-142/T + 0,635$
e_N^{Mo}	$-33,2/T + 0,0064$
$r_N^{Mo,Mo}$	$-5,57/T + 0,0025$

A Pascal computer program was written to calculate the solubility of nitrogen in alloys of varying composition at different temperatures and nitrogen pressures. The parameters given in Table I were used to find f_N, the fugacity of the nitrogen, which is defined[17] as

$$\log f_N = \sum_j e_N^j[\%j] + \sum_j \sum_k r_N^{j,k}[\%j][\%k]$$

for the particular set of interaction coefficients used. The value of f_N was then used to find the amount of nitrogen (mass percentage) in the alloy using the available expression for the solubility of nitrogen in pure iron, and the expression

$$f_N = \frac{[\%N]_{Fe}}{[\%N]_{alloy}}.$$

Nitrogen Content Based on F*A*C*T's EQUILIB Program

F*A*C*T[20] is a computer system for thermochemical calculations. This system offers many services, and has one of the most comprehensive collections of data on pure inorganic compounds, as well as non-ideal solutions. It can be accessed online (by means of a personal computer equipped with a modem) from McGill University in Montreal, Canada[21]. F*A*C*T's EQUILIB program calculates the equilibrium products of complex multiphase chemical reactions constrained by, for example, temperature and pressure. This program is based on Eriksson's SOLGAMIX program[22], which uses free-energy minimization to calculate the equilibrium composition of solid, liquid, and gaseous systems. Non-ideal solution models can be incorporated in this program. In the present investigation, F*A*C*T's liquid iron-dilute solution database was used to calculate the nitrogen content of molten steel.

Trial Melts

Three alloys were chosen for study, with the charge compositions given in Table II. The maximum nitrogen content would, on the basis of the coefficients given in Table I, be expected to *decrease* from the first to the second alloy, and *increase* from the second to the third alloy. The experimental alloys were melted at approximately 1500°C in a vacuum induction furnace, which was back-filled with nitrogen gas to an absolute pressure of about 0,5 atm. The nitrogen was introduced in the form of nitrided ferromanganese, and enough of the latter was added to ensure that up to 0,5 per cent nitrogen by mass was available for alloying. It was expected that nitrogen in excess of the thermodynamic limit would bubble off into the furnace chamber.

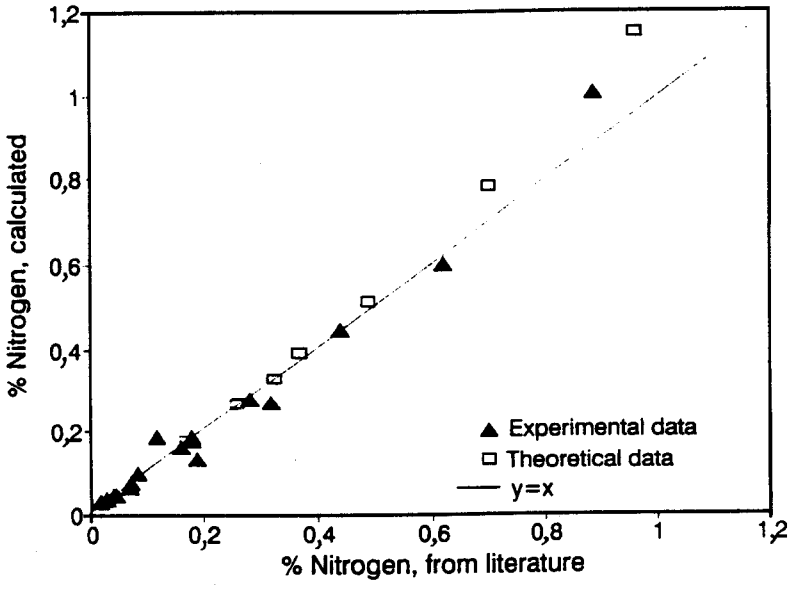

Figure 1–Nitrogen values for various alloys reported in the literature plotted against the results of the present model when applied to the same data

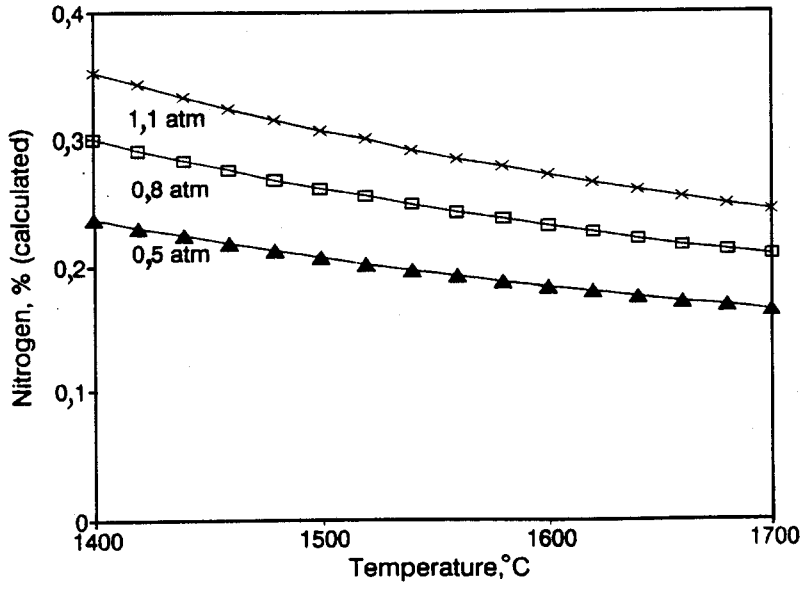

Figure 2–Solubility of nitrogen as a function of temperature and pressure, calculated for an Fe–17%Cr–7%Mn–3%Ni–3%Cu–0,4%Si–0,035%C alloy using the present model

7. TURAN, Y.N., and KOURSARIS, A. Nitrogen-alloyed austenitic stainless steels and their properties. *J. S. Afr. Inst. Min. Metall.*, vol. 93, no. 4. 1993. pp. 97–104.
8. TOCHOWICZ, S., SIWKA, J., and JOWSA, J. Alloying steel with nitrogen from gas phase in high-pressure plasma reactor. *Steel Res.*, vol. 64, no. 3. 1993. pp. 165–170.

The actual ingot compositions (excluding nitrogen) were entered into the F*A*C*T program and database, together with an excess of nitrogen, and the equilibrium physical states of the systems were calculated.

Table II

Nominal charge compositions of iron-based experimental melts, % by mass

Melt number	Cr	Mn	Ni	Cu	Si	C	N
VF 965	17,5	7	3	0	0,4	0,1	0,5
VF 967	17,5	7	3	3	0,4	0,1	0,5
VF 968	17,5	10	3	3	0,4	0,1	0,5

Table III

Actual compositions of iron-based experimental melts, % by mass

Melt number	Cr	Mn	Ni	Cu	Si	C	N
VF 965	17,5	6,75	3,04	0,006	0,42	0,11	0,36
VF 967	17,0	6,70	3,12	3,08	0,36	0,11	0,40
VF 968	17,6	10,1	3,04	3,05	0,41	0,11	0,41

Results

The actual ingot compositions are given in Table III.

Figure 1 shows the predictions of the Pascal computer program plotted against nitrogen values (either experimental or theoretical) obtained from the literature. It is evident that the program and interaction coefficients used are accurate up to about 0,6 per cent nitrogen, and slightly optimistic at greater nitrogen contents. The program correctly predicted that the solubility of nitrogen in a hypothetical Fe-17%Cr-7%Mn-3%Ni-3%Cu alloy decreased with an increase in temperature and increased with an increase in pressure (Figure 2). A slight decrease in solubility with an increase in copper content was indicated (Figure 3).

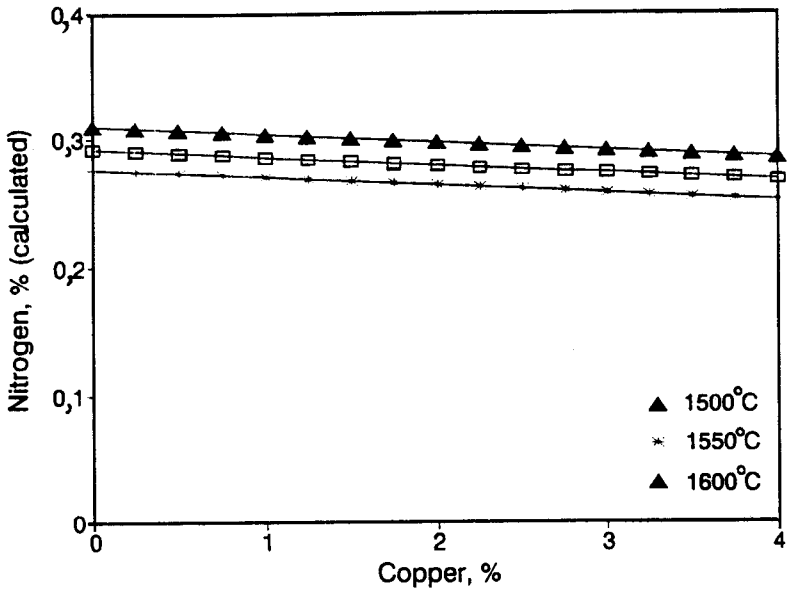

Figure 3–Solubility of nitrogen as a function of copper content and temperature, calculated for an Fe–17%Cr–7%Mn–3%Ni–0,4%Si–0,035%C alloy under 1 atm. of nitrogen using the present model

Table IV

Comparison of the theoretical techniques with the actual results

Alloy	Program (low)	Program (high)	F*A*C*T (Low)	F*A*C*T (High)	Actual
VF965	0,198	0,237	0,240	0,289	0,36
VF967	0,179	0,214	0,218	0,261	0,40
VF968	0,218	0,260	0,273	0,328	0,41

9. WADA, and PEHLKE, R.D. Nitrogen solution and titanium nitride precipitation in liquid Fe–Cr–Ni alloys. *Metall. Trans. B*, vol. 8B. Sep. 1977. pp. 443–450.
10. PEHLKE, R.D., and ELLIOTT, J.F. Solubility of nitrogen in liquid iron alloys. *AIME Trans.*, vol. 218. Dec. 1960. pp. 1088–1101.
11. CHIPMAN, J., and CORRIGAN, D.A. Prediction of the solubility of nitrogen in molten steel. *AIME Trans.*, vol. 233. Jul. 1965. pp. 1249–1252.
12. POMARIN, Y.M., and GRIGENKO, G.M. Equation of the calculation of nitrogen solubility in iron melts. *Izv. AN USSR. Metally*, no. 4, 1989. pp. 40–45. (Available in translation as *Russ. Metall.*, no. 4. 1989. pp. 33–38.

The predictions made by the use of interaction coefficients and those made by F*A*C*T are compared in Table IV with the actual nitrogen contents of the three melts. Both F*A*C*T and the Pascal program were run for various temperatures and pressures, since the melt parameters were not known exactly. The temperature range was taken to be between 1450 and 1500°C, and the nitrogen pressure between 0,4 and 0,5 atm. The 'low' estimates in Table IV were obtained with the higher temperature and lower nitrogen pressure, while the 'high' estimates were calculated from the lower temperature and the higher nitrogen pressure. An example of the dialogue entered into with the F*A*C*T system is reproduced in the Addendum. It should be noted that samples VF965 and VF967 had a chromium content that was extrapolated from the suggested composition range, while sample VF968 had both chromium and manganese contents out of the suggested range.

Discussion

It is evident that the theoretical results from both the F*A*C*T and the Pascal programs indicate that the addition of 3 per cent copper to the base alloy should lower the solubility of nitrogen by about 0,02 and 0,04 per cent, depending on temperature and pressure. This may not be a significant decline, given the typical composition ranges specified in industry. However, the solubility can be restored, and even increased, by further additions of manganese. The additional 3 per cent manganese in the third alloy, for example, was able to raise the theoretical solubility of nitrogen by at least 0,04 per cent. However, the addition of manganese would lower the stacking fault energy, which is considered to be undesirable from the point of view of good formability. More significant changes with composition were found at the lower temperature and higher pressure, indicating once again that the temperature and pressure of the melt dominate minor variations in composition. It is, however, also evident that the three sets of results do not agree very well. The F*A*C*T system predicts nitrogen contents that are about 20 to 25 per cent higher than those predicted by the method of interaction coefficients, which, as shown in Figure 1, is quite accurate. This may be due to the paucity of advanced thermochemical data for the effect of manganese in solution in liquid steel[13].

The actual nitrogen contents are considerably higher than those predicted by either theoretical method. The discrepancies between the various results may be due to one or more of the following factors.

- The melts did not reach equilibrium in the induction furnace. (This verdict was also reached by Turan and Koursaris in their investigations on the subject[7].)
- The temperature and pressure of the melts fell outside the assumed envelope. This would be true if the temperature was less than 1450°C and the pressure fluctuations were greater than 0,1 atm. during the melting process.
- The interaction coefficients were not sufficiently accurate. The coefficients used were determined from ternary Fe–N–X systems, and were assumed to remain the same in a complex alloy[11]. This assumption may not hold for the complex alloys studied here.
- Insufficient interaction coefficients may have been used. The second- and third-order interaction coefficients are of much smaller magnitude than the first, and therefore are usually ignored for dilute solutes. For a high degree of accuracy, more of them should be included.

13. HILLERT, M., and QIU, C. The effect of N and Mn on equilibria in austenitic stainless steels, illustrated with computer calculations. *Applications of Stainless Steel '92*. Nordberg, H. and Björklund, J. (eds.). Jernkontoret (Sweden), 1992. pp. 13-24.
14. RAWERS, J., BENNETT, J., DOAN, R., and SIPLE, J. Nitrogen solubility and nitride formation in Fe-Cr-Mn-Ni alloys. *Acta Metall. Mater.*, vol. 40, no. 6 1992. pp. 1195-1199.
15. CORTIE, M.B., WELLBELOVED, D., KINCER, M., and LULA, R.A. Experimental austenitic stainless steels containing 7% Mn, 2% Ni, and up to 4% Cu. *High Manganese Austenitic Stainless Steels*. Lula, R.A. (ed.). ASM, 1993. pp. 177-185.
16. GASKELL, D.R. *Introduction to metallurgical thermodynamics*. New York, McGraw-Hill, 1973.
17. *Steelmaking data sourcebook*. New York, Gordon and Breach Science Publishers, 1988.
18. TURAN, Y.N., and KOURSARIS, A. Nitrogen alloying of AISI 310S in an induction furnace. *J. S. Afr. Inst. Min. Metall.*, vol. 92, no. 3. Mar. 1992. pp. 79-83.
19. HUMBERT, J.C., and ELLIOTT, J.F. The solubility of nitrogen in liquid Fe-Cr-Ni alloys. *AIME Trans.*, vol. 218, 1960. pp. 1076-1088.
20. THERMFACT (447 Berwick Avenue, Mont-Royal, Quebec, Canada H3R 1Z8). *Facility for the analysis of chemical thermodynamics*.
21. THOMPSON, W.T., BALE, C.W., and PELTON, A.D. Interactive computer tabulation of thermodynamic properties with the F*A*C*T system. *J. Met.*, Dec. 1980. pp. 18-22.
22. ERIKSSON, G. Thermodynamic studies of high temperature equilibria. XII. SOLGAMIX. a computer program for calculation of equilibrium compositions in multi-phase systems. *Chem. Scripta*, vol. 8. 1975. pp. 100-103.

- ➤ Some of the data used by the F*A*C*T database have not been verified experimentally over the particular range of composition that is of interest here.

Conclusions

The method of interaction coefficients predicted nitrogen contents that were lower than the experimental results, and the discrepancies between the two sets of results are thought to result from the melts not reaching equilibrium at the target temperatures and pressures. The results produced by the F*A*C*T database in this case were consistently on the high side. However, either theoretical method appears to be sufficiently accurate for a conservative prediction of nitrogen content.

The decrease in solubility due to the addition of copper is small, and can be corrected by an increase in the manganese content. In order to ensure maximum nitrogen solubility, melting must be carried out at the lowest possible temperature and the highest possible nitrogen pressure. The effects of the two latter factors (particularly temperature) influence the solubility very strongly, and will often outweigh the effect of alloy composition. Finally, it has been shown that substantially higher nitrogen contents can be obtained in an induction furnace in practice, provided that non-equilibrium conditions pertain. The latter can be facilitated by the addition of the nitrided ferro-alloy towards the end of the melting process, and allowing just enough time for it to melt before the alloy is cast.

Addendum: Sample F*A*C*T Dialogue

The numbers in the first line refer to moles of reactant. The particular run shown is for the composition of VF968 at 1500°C and 0,4 atm. N_2. The 'C's printed alongside the results for Cr and Mn are to warn the user that the thermodynamic data for these elements have been found by extrapolation.

```
338.5 Cr + 183.8 Mn + 48.8 Cu + 14.2 Si +
8.3 C + 71.4 N + 1158.5 Fe =

   26.023  mol (1.0000 N2)
           (1773.15 K,0.40000 atm, gas)
 + 1812.9 mol (0.63904    Fe
           + 0.18672      Cr    C
           + 0.10139      Mn    C
           + 0.28187E-01  Ni
           + 0.26919E-01  Cu
           + 0.78329E-02  Si
           + 0.53379E-02  N2
           + 0.45784E-02  C)
           (1773.15 K,0.40000 atm, Fe_liq.) ◆
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Evaluation of sulphur assays

The third in the series of a 'Sulphur Assay Round Robin' has recently been completed. The aim of these investigations, initiated by the UCT-SENMIN Research Group in the Department of Chemical Engineering at the University of Cape Town in 1990, is to ascertain the consistency of sulphur assays performed routinely at different laboratories in South Africa. The five participating laboratories at present are as follows: Anglo American Research Laboratories, Gencor Research Laboratories, Mintek, Karbochem, and the UCT-SENMIN Research Group.

Samples of concentrates, feeds, and tailings generated in pyrite batch flotation tests were dried, blended, riffled, split, and sent to each laboratory. Various methods were used to assay for sulphur at the different laboratories. The results of the assays for total sulphur and sulphide sulphur were collated, and a report was compiled and distributed to the participants.

One of the participating laboratories reported the concentrate assay to be out of range by one standard deviation. Their procedure was checked, and the problem was diagnosed and corrected. This clearly demonstrated the value of the exercise.

It has been decided to repeat this exercise on an annual basis, and we extend an invitation to other interested laboratories to participate. For further information, please contact D.J. Bradshaw, UCT-SENMIN Research Group, Department of Chemical Engineering, UCT, Rondebosch, 7700. Fax (021) 650-3775.