

Recycling Technologies for Metal Processing - An Australian Perspective

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Following the trends around the world in the 1990's, Australia has been promoting recycling as a means to reduce wastes and at the same time improve the economics of metal processing. Of significance to the metal processing industry is the recycling of steel and aluminium, mostly from cans collected from households. The recycling of cyanide during gold processing has also been evaluated extensively, involving many R&D activities currently conducted in several laboratories and commercial plants in Australia. This paper presents an overview of the above issues, evaluating facts and data collected on metal recycling. The technologies currently developed and evaluated for cyanide recycling are also discussed.

Keywords: metal recycling, cyanide recycling, recycling technologies

Introduction

The mineral and metal processing industry in Australia is facing more pressing issues related to cost cutting to improve the overall process economics. One of these issues is concerned with the recycling of metals and reagents used for processing them.

Over the last decade, recycling has been the key issue facing metal producers in Australia, although in some cases the cost of recycling is the only factor affecting its implementation. Of most significance is the recycling of aluminium and steel cans, mostly from domestic and kerbside recycling systems, which have been introduced in Sydney, NSW since the late eighties (Nolan, 1998). Substantial support from the community has resulted in more than 85% participation rate, with more than 18% of domestic waste is recovered for recycling. The systems in place collect green wastes (plant matters), glass, paper, aluminium cans and plastic, which are then sent to recyclers for further processing.

Another emerging trend is also observed during the processing of gold. In this case, recycling of cyanide has been long considered as the better environmental management option, aiming to reduce the gold processing cost. The technologies adopted for recycling cyanide are based on acidification of cyanide liquors or pulps to convert soluble cyanide into hydrogen cyanide (HCN), volatilization of the HCN and regeneration of NaCN for recycling by absorption into caustic NaOH. In most cases the AVR technique is used in conjunction with ion exchange resins, which remove cyanide from the liquors and render the wastewater free of cyanide (Tran et al, 2000).

This paper presents the Australian perspective on metal and cyanide recycling, showing past and present activities.

Particular emphasis will be placed on the recycling of aluminium and steel cans and the AVR-ion exchange and other technologies currently being evaluated in Australia.

Metal Recycling in Australia

Over the last decade, a significant increase in public awareness on environmental issues has brought with it a massive increase in recycling activities in Australia (Planet Ark, 2001). The history of metal recycling however started with BHP Steel's scrap steel recycling in 1915. In 1975, Canterbury Council was the first municipality to use magnetic separation to recover steel wastes, including cans. Over 20 years ago, Comalco (and many other companies) established nationwide campaigns to promote aluminium recycling to the general public with its "Cash-for-cans" programs. They targeted at community and children groups to collect and sell aluminium cans to collection centers, raising funds for charity projects. The kerbside recycling schemes, initially started in Sydney, was introduced in the late 1980's. This scheme allows separation of household items such as paper, glass, aluminium and steel cans, plastic, etc., which are put in bins left for collection weekly or bi-weekly at kerbside then sold to recyclers for processing. A National Kerbside Recycling Strategy was endorsed by the Australian & New Zealand Environment and Conservation Council in 1992 to promote voluntary recycling and call for commitments at all level of industry.

The largest source of recycled aluminium and steel is from household waste collection. In 1997, on average for a population of 4.5 million people in Sydney, the rate of recycling in the Sydney region is 3.5 kg per household per week at a cost of \$27.70 per household per annum or \$141/ tonne. The highest component values are glass

(40%) and paper (41%). Aluminium and steel come next at 4.3% and 1.6%, respectively.

An unaccounted but large proportion of brass and copper has also been collected, mostly from industrial disposal. These are generally handled by scrap metal dealers such as Simsmetals who purchase and on-sell them to smelters around the world.

Aluminium Can Recycling

Kaal is the largest recycler of aluminium in Australia covering around 90% of the market (Kaal, Australia, 2001). The material recycled to Kaal plants includes beverage containers, extrusion scrap aluminium, cable aluminium, and other sources. The price paid for aluminium scrap is 50-60% of the London Metal Exchange aluminium prices.

In 2000, Australia recycled over 25,700 tonnes of aluminium cans (over 1.6 billion cans), an amount totaling 67% of the cans used. The recycling plant only uses a fraction of energy to process recycled cans, compared with the production of new cans made from raw materials. In general, twenty aluminium cans can be recycled using the same energy required to produce one can from raw materials. The value of all aluminium cans available, of which 67% was recycled last year, is equivalent to \$A 15M to be paid by "Cash-for-Cans" centers around Australia.

The aluminium drink cans collected for recycling are first sorted and then pressed into bricks. These are then transported to Kaal processing plant in Yennora, NSW and fed into the remelt furnaces and melted at 800 °C. The molten aluminium is casted into ingots and sent to rolling mills to produce new sheets.

Steel Can Recycling

Steel cans on the other hand are sold to BHP, the main buyer of scrap iron, at a price (of baled steel cans) of around \$70-80/tonne. The national average for steel can recycling was 28% in 1997, which rose to 38% in 2000. This is equivalent to 640 million steel cans (used for as food container). The energy required to make new steel from recycled cans uses 75% less energy than producing steel from raw materials. The recycled steel cans are converted into car bodies, railway girders, bicycles and new cans. Recycled steel is used as part of the feed to steelmaking or in most cases into scrap melting furnaces.

Cyanide Chemistry and Environmental Issues

During the processing of gold ores by cyanidation, several cyanide-soluble minerals also react with cyanide forming base metal cyanides, from weak complex such as zinc cyanide to very strong and stable cyanides such as ferri- and ferrocyanide.

Copper oxide minerals such as azurite ($\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$) and malachite ($\text{Cu}_2\text{CO}_3(\text{OH})_2$), cuprite (Cu_2O), tenorite

(CuO), chalcocite (Cu_2S) and covellite (CuS) are all very soluble and leached at a high rate in dilute cyanide liquors. Other complex sulphides such as bornite (Cu_5FeS_4), chrysocolla ($\text{Cu}_2\text{H}_2\text{Si}_2\text{O}_5(\text{OH})_4$) and particularly chalcopyrite (CuFeS_2) are less soluble during gold extraction.

Other sulphides of zinc (sphalerite), iron (marcasite FeS_2 and pyrrhotite FeS), antimony (stibnite) and nickel (iron-nickel sulphide, pentlandite) also consume cyanide, forming various metal cyanide species. Some of these (such as zinc and cadmium cyanide) are weak and easily break down while others (such as ferro- and ferricyanide) are very stable in solution.

Of interest to plant practice are those cyanide species bound with zinc, cadmium and nickel cations, including a proportion of copper cyanides. These are classified as weak-acid-dissociable cyanide (CN_{wad}), which is easily dissociated by acidification forming HCN. Due to the instability of these base metal cyanides, the NSW-EPA has imposed a limit of 20 CN_{wad} in tailing dams for new operations. Cyanide species of iron (ferrocyanide and ferricyanide) are more stable in solution and can form insoluble double-salt complexes of copper-iron and zinc-iron cyanide at $\text{pH} < 6.5$ in the presence of zinc and copper cations.

Another issue of significance to plant practice is the formation of thiocyanate when the above sulphide minerals dissolve in cyanide. Although there is no government legislation within Australia restricting the disposal of thiocyanate at present, the detoxification required for the treatment of cyanide wastes would consume oxidising chemicals used for cyanide destruction.

The latest trend in cyanide management involves the treatment of free and complex cyanide to recover cyanide (CN^-) for recycling. The process involves the conversion of free and complex cyanide to produce sodium cyanide (NaCN) via acidification-volatilisation-regeneration (AVR) steps. In some cases, adsorption onto ion exchange resins is also considered.

Cyanide Recycling – Process Considerations

General

Processes based on ion exchange resins and AVR circuits have the unique advantage of recovering cyanide to offset the cost of reagents used in these processes. The process of cyanide recovery from solutions by acidification, volatilisation and regeneration has been known since 1929. It was first known as the Mille Crows Process, and since the 1970's after developments by CANMET and McNamara, has been referred to as the AVR process (Tran et al, 2000).

The AVR circuit involves acidification of the cyanide liquors or slurries to lower the pH from ~10 to pH~3-5 to convert free cyanide and weak complexes (complexes of

Zn, Cd, Ni) to HCN which is then volatilised by passing air bubbles through the liquor or pulp. The air/HCN stream is then scrubbed in a lime slurry or NaOH solution to convert HCN back to sodium cyanide for recycling.

A considerable amount of effort has been spent to improve its performance since its early development. It has become accepted by the industry as an option for treating moderate or strong cyanide liquors (over 500 ppm CN_{WAD}). However, copper will be precipitated as copper cyanide (CuCN) during the acidification stage which is an unsaleable product and binds up a third of the available cyanide complexed with the copper, lowering the cyanide recovery. Questions on costs and efficiencies still create doubts, which prevent its application for the treatment of dilute cyanide liquors.

Cyanide recovery has also currently been used in several plants in America, based on a process developed and marketed as the Cyanisorb process. Cyanide recovery has also been seriously considered in operations where the use of cyanide is prohibitively high due to the presence of cyanide-consuming copper minerals. Several technologies have been proposed and tested over the last decade, aiming to overcome the technical problems encountered during the processing of copper-gold ores. These technologies incorporate a copper processing and recovery step, and in some cases, a pre-concentration stage to raise the copper levels of the treated liquors. Cyanide is mostly recovered via HCN formation, stripping and absorption into caustic or lime, forming sodium cyanide or calcium cyanide for recycling.

One of the most critical aspects of cyanide recovery plants is the control instrumentation strategy, which has to be put in place to monitor HCN emission. Plants have to be designed to shut down automatically if a high level of HCN is detected. At May Day Mine, several monitors were installed around the processing plant and alarms will sound as the level of HCN in the air around the plant reached 10 ppm (10 mg per m^3 of air). The plant would automatically shut down when the HCN level reached 80-100 ppm in air around the plant.

Another critical aspect of cyanide recovery is related to the efficiency of stripping HCN from the pulp or liquor. The Cyanisorb process relies on the use of stripping tower packed with plastic media (50-75 mm dia) to improve the HCN recovery efficiency. At May Day Mine, a similar design was also used to effectively handle 100 tonne cyanide per hour through the plant. Air at 10,000 m^3/h can be effectively passed through the stripping and recovery column to handle the above cyanide throughput.

The Cyanisorb Process

The Cyanisorb process described in several US patents (US 4,994,243 and 5,078,977 and 5,254,153) are owned by Coeur d'Alene Mines Corp and is now marketed by Unifield Engineering (USA). The process is slightly different from the original AVR circuits in that clear solutions or slurries are processed at near neutral pH.

Following its first operation at the Golden Cross Mine in New Zealand in the early 1990's, other plants were subsequently built in South America (Cerro Vanguardia, October 1998; Rio Tinto Brazil's Rio Paracatu Mineração S.A, March 1998). Details of these operations are well publicised at the Unifield Engineering's website (www.cyaniderecovery.com).

The advantages of the Cyanisorb process are:

- Cyanide can be recovered and re-used, rendering barren liquors or pulps containing less than 10 ppm CN_{WAD} .
- Heavy metals (except copper) are removed as hydroxide. Iron is removed as cyanide double salts.
- Reagents used (air, lime or caustic and sulphuric acid) are cheap and readily available.
- In most cases, the cost of recovery is cheaper than the cost of importing cyanide into the plant operations.
- Several plants in South America are using this technology.

Disadvantages include:

- Cyanide associated with SCN is not recovered by acidification alone,
- CuCN is produced which lowers the cyanide recovery efficiency if copper cyanide is present at high levels in the treated pulps or wastewaters. CuCN is not a readily saleable product.
- The capital cost is generally higher than other oxidation processes. The return in investment is dependent on the savings / differences between the chemical costs used for recycling versus the cost of importing cyanide into operations.
- Plant operations require proper control on HCN emission.

The MNR (SART) Process

The MNR (or SART) process which was developed by Metallgesellschaft Natural Resources (Germany) involves the sulphidisation (using NaSH) and acidification (to less than pH 5) of copper cyanide rich liquors to precipitate copper as synthetic chalcocite (Cu_2S).

After filtration, the liquor is re-causticised to produce caustic cyanide or acidified further to form HCN gas and recovered via absorption columns (Davis *et al*, 1998; Dreisinger, 1998). The precipitate is a marketable copper product and can be blended with other copper flotation concentrates produced on site. Possible contamination of other base metal sulphide formed during precipitation of copper cyanide (such as zinc) does exist which might

present heavy penalties on concentrate sale if contaminants are higher than product specifications (Dreisinger, 1998). Material handling of the Cu(I) sulphide and potential co-precipitation of CuCN and CuSCN are also issues which require serious considerations in plant design.

The MNR (SART) process is currently tested by Newcrest Mining at its Telfer Mine. The process is particularly applicable for this operation as existing counter-current decantation operations are in place treating a high copper-gold concentrate. More details on the SART process as tested by Fleming and his co-workers at Lakefield Research labs were published at Randol 98.

Henkel's Solvent Extraction – MNR Process

The Henkel SX-MNR process, which was tested at a pilot scale at Mintek (South Africa) is more applicable for treating clear and preferably concentrated copper-gold cyanide liquors to achieve a high efficiency in precipitation and material handling. In this process, Henkel has proposed a solvent-extraction route to concentrate copper to 30-40 g/L (in 50 g/L total cyanide, 10 g/L NaOH) from dilute liquors containing less than 1 g/L of copper and 1.7 g/L total cyanide (Davis *et al*, 1998). The process uses Henkel's XI-78 reagent, comprising of Alliquat 336, a quaternary amine modified by a phenol for separating copper from copper-gold cyanide liquors which is then recovered using the MNR precipitation technique.

Gold is also extracted from the solution using Aurix 100 medium base resin (a guanidine-based resin manufactured by Henkel) or Dowex Minix resin which are selective for gold over copper and other base metals.

Resin Technologies for Cyanide Recovery

Resins have been used since the 1980's to recover gold from gold cyanide leach liquors in South Africa at Golden Jubilee Gold Mine (Fleming *et al*, 1984; 1990) and earlier in the former USSR states (Bolinski and Shirley, 1996; Marsden and House, 1992). The earlier processes relied on basic eluants such as thiocyanate (SCN), chloride, hydroxide to remove gold cyanide from the loaded resin for further processing. However, in the presence of base metal cyanide complexes in the liquor, sulphuric acid is also used to strip these complexes off the resins. The acid elution employed in several latest processes destroys the cyanide complexes, regenerating cyanide for recycling via HCN gas.

The AugMENT Process

The AugMENT process (Fleming, 1998) relies on commercial strong-base resins for recovering and concentrating the copper cyanide. The resin is first impregnated with CuCN precipitate to produce an efficient adsorbent for free cyanide and soluble copper cyanides. After loading, the resin is then stripped with a copper cyanide/caustic eluant (10-70 g/L Cu, 10 g/L

NaOH, total CN/Cu ratio of 3.5-4.0:1). Gold has to be recovered prior to copper electrowinning and cyanide recovery.

As part of the AugMENT process, copper is produced from Cu(I) cyanide using Dupont membrane cells. The patented membrane cell utilises a sodium-selective ion-exchange membrane (Nafion 417, Dupont) to electrowin copper and regenerate cyanide at the cathode. The membrane is necessary for the separation of the anolyte and catholyte to prevent oxidation of cyanide to cyanate. Cyanide is recovered via an AVR circuit, where the CuCN is precipitated and re-dissolved in the loaded catholyte ahead of the electrowinning circuit.

The Vitrokele Process

Another resin technology, the Vitrokele process based on a Resin-In-Column circuit, was successfully applied at Connemara, Zimbabwe for processing gold from oxidized ores using heap leaching (Satalic, 1996). In this process, gold cyanide was uptaken onto resin columns from leach liquors, which contain low levels of other base metals. Gold is eluted by 0.5M zinc cyanide at 60 deg.C and recovered by electrowinning using the Golden Jubilee's electro-elution circuit.

During the period from July 1997-June 1998 it was tested on copper-gold ores at Imperial Mining's May Day Mine, 120 km south of Cobar, NSW, under the sponsorship of an IR&D syndicate scheme (Paterson and Jenkins, 1997). At May Day Mine, the Vitrokele technology was used to process (at 60 m³ per hour) a vat-leach liquor containing gold and copper cyanide produced from 250,000 tonnes of agglomerated ore that graded 2.2 g/t gold, 15.2 g/t silver and 0.12% copper. The leach liquor contained 2-3 ppm Au, 25 ppm Ag, 50 ppm Zn, <1 ppm Fe and 200 ppm Cu. As reported earlier (Davis *et al*, 1998) a strong cyanide solution (100g/L NaCN, 10 g/L NaOH) was used to elute copper from the resin. This step produced a copper liquor in a highly concentrated sodium cyanide background, which was then acidified to precipitate copper as CuCN. Apart from the loss of cyanide tied up with the CuCN, the AVR circuit had to handle a massive amount of HCN generated unnecessarily from the acidification of the NaCN eluant. Gold was eluted from the resin columns and recovered from an electro-elution circuit, similar to the operation at the former Golden Jubilee plant, South Africa. Several technical problems were encountered during the processing which led to the abandonment of the Vitrokele process at May Day Mine.

Imperial Mining abandoned its effort in promoting the Vitrokele process by the end of 1998, due to the heavy cost incurred at May Day Mine.

The Elutech Process

Over the period from December 1998 to April 1999, approximately 21,000 m³ of the pregnant liquor containing 0.6-1.0 ppm Au, 5-10 ppm Ag, 60-150 ppm Cu 10-15 ppm Zn and approximately 100 ppm free cyanide

was treated at May Day Mine using Elutech's adsorption, base metal elution as well as cyanide recovery processes (The plant conditions were developed from a laboratory program conducted at UNSW under a research contract).

The plant consists of adsorption columns that hold 2.5 m³ of commercially available strong base ion exchange resins that operate on adsorption/elution cycles sequentially. The plant employed a telluret-packed column for HCN stripping using air (at maximum 10,000 m³/hour) in counter current contact with the stripped solution. The stripped HCN gas is then absorbed into caustic using another telluret-packed column operated in counter-current mode between the stripped HCN and the caustic phase.

During the adsorption stage, all metal cyanide complexes are loaded on to the resin without much selectivity. Then the water wash that follows the adsorption stage removes any non-adsorbed materials from the resin bed and prepares the resin for base metal elution. During the base metal elution step, the resin is flushed with an oxidative-acid eluent that converts the base metal cyanide to their respective sulphate forms.

The eluent is circulated through the resin bed for a sufficient time to complete the elution. During the elution, the cyanide attached to the metal cyanide species adsorbed on the resin is converted into HCN and comes off the resin as dissolved HCN in the eluent as well as HCN gas (when the eluent is saturated with HCN). This gas-liquid mixture that exits the resin bed is fed to an HCN stripping column where the HCN gas is separated from the eluent using air, before the eluent is re-circulated to the resin column. The HCN gas that is generated in this process is then adsorbed in diluted NaOH solution (at a pH of 13) to produce NaCN, which is recycled. After the elution is completed, the resin bed is given another water wash to remove the remaining eluent before the resin is subjected to adsorption in the next cycle.

Of all the metals that are loaded during the adsorption cycle, only base metals are eluted off the resin during the elution stage, leaving the gold and silver that are loaded onto resin intact. This allows gold and silver to be sufficiently built up on the resin (>10 kg precious metals /m³ resin), and most importantly, not to be co-eluted during the base metal elution. The gold elution uses a hot (60 °C) zinc tetra-cyanide solution over a period of 48 to 60 hrs. At the end of the gold elution stage, the resin bed is thoroughly saturated with zinc tetra-cyanide and has to be regenerated before being subjected to the next adsorption/elution cycles.

The plant layout and flowsheet are shown in Figs. 1 and 2 respectively. The processing plant is separated from the leaching operation, conducted on vats, which are not shown in this photo. The flowsheet only represents the loading and stripping operation of the Resin-In-Column circuit.

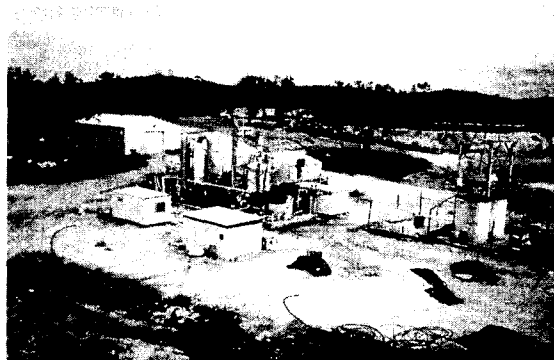


Fig. 1: Photo of May Day Resin Plant

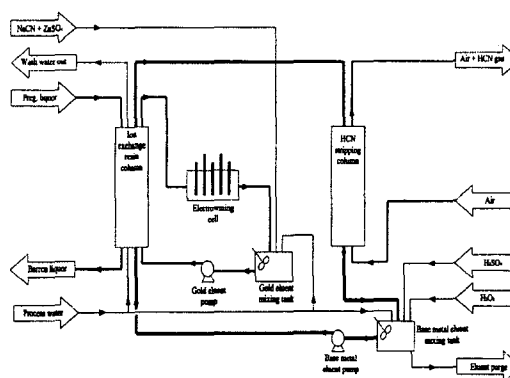


Fig. 2: Flowsheet of May Day resin plant

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References

- Bolinski, L. and Shirley, J. (1996) Russian Resin-In-Pulp technology, current status and recent developments, Randol Gold Forum '96, pub: Randol International, 419-423.
- Davis, M.R., Sole K.S., Mackenzie, J.M.W. and Virnig, M.J. (1998) A proposed solvent extraction route for the treatment of copper cyanide solutions produced in leaching of gold ores, Alta Copper Hydrometallurgical Forum, Brisbane Australia, October.
- Dreisinger, D.B. (1998) The MNR or SART process applied to heap leach solutions arising from cyanide treatment of copper-gold ores, paper presented at Metallurgical In-House seminar, Feb 2 - 4 (Orange, NSW).

- Fleming, C.A. (1998) The potential role of anion exchange resins in the gold industry, EDP Congress 1998, ed: Mishra, B., pub: TMS-AIME, Warredale, PA, 95-117.
- Fleming, C.A. and Cromberge, G.(1984) The elution of auro-cyanide from strong and weak base resins, J. South Afr. Inst. Min. Metall., 84(9), 269-280.
- Fleming, C.A. and Cromberge, G. (1984) Small scale pilot-plant tests on the resin-in-pulp extraction of gold from cyanide media, J. South Afr. Inst Min. Metall., 84(9), 369-378.
- Fleming, C.A. and Seymore, D. (1990) Golden Jubilee RIP Plant, Randol Gold Forum, Squaw Valley '90, pub: Randol International, 237-241.
- Kaal, Australia Pty Ltd,
www.brba.com.au/members/kaal.htm
- Lawson, P.J., Dicoski, G.W. and Rideout, J.A. (1993) Gold and silver selective anion exchange resins, Proc. Randol Gold Forum, Beaver Creek '93, Sept 7-9, Vail Valley, Colorado, pub: Randol International, 301-308.
- Mackenzie, J.M.W. (1993) Henkel IX resins and Henkel LIX 79 solvent for gold recovery from alkaline cyanide leach solutions, Randol Gold Forum, Beaver Creek '93, Sept 7-9, Vail Valley, Colorado, pub: Randol International, 287-292.
- Marsden, I and House, I., (1992) Chemistry of gold extraction, pub: Hollingsworth, London.
- Nolan-ITU Pty Ltd 91998), Kerbside recycling in NSW, Supply, Demand and Costs, pub: NSW-EPA, <http://www.planetark.org/recycling>
- Parker, B (1998) Vitrokele resin technology for copper-gold ore processing, Newcrest Mining In-house seminar February 2-4, Orange, NSW.
- Paterson, M.A. and Jenkins, A.R. (1997) Vitrokele resin technology for the recovery of complex and free cyanide, in proceeding of Workshop on Management of Cyanide in Mining, 14-16 April, Perth, WA.
- Planet Ark, 2001, www.planetark.org
- Satanic D.M., Spencer, P.A., Paterson, M.R. (1996) Vitrokele: commercial application in the gold industry, Proc. AusIMM Annual Conf., 167.
- Scerescini, B. and Staunton, W.P., (1991) Copper cyanide in the treatment of high copper gold ores, proc. AusIMM Extractive Metallurgy Conf., Perth 2-4 October, 123-125.
- Tan, E. (2000) Stability of Copper/Iron cyanide double salts, fourth year undergraduate thesis, School of Chemical Engineering and Industrial Chemistry, The University of New South Wales.
- Tran, T. and Hsu, Y-J. (1996) Selective recovery of gold from copper gold cyanide liquors by zinc cementation, Minerals Engineering, 9(1), 1-13.
- Tran, T., Nguyen, H.H. and Wong, P.L.M. (1997) A kinetic study on the cementation of gold from cyanide solutions onto copper, Hydrometallurgy, 46, 55-69.
- Tran, T., Lee, K., Fernando, K. and Rainer, S., (2000), The use of ion exchange resin for cyanide management during the processing of copper-gold ores, Proc. of Minprex 2000 Congress, Melbourne, Australia, 10-13 September 2000, pub: AusIMM, Melbourne, Australia, 207-216.
- Tran, T., Lee, K., Fernando, K. and Lucien, F., (2001), Use of ion exchange resin for the treatment of cyanide and thiocyanate during the processing of gold ores, in: Cyanide – Social, Industrial and Economic Aspects, ed: Young, C., Twidwell, L. and Anderson, C., TMS Meeting, New Orleans, Feb 12-15, 2001, pub: TMS, Warrendale, Pennsylvania, USA, 289-302.