CONTRIBUTIONS OF CHEMISTRY TO SUSTAINABILITY IN CHINA

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Summary

Conservation in resource utilization and preservation and control of the environment have been envisioned as the significant roles that chemistry can play in life support systems and sustainable development. These two roles are often interconnected. For instance, the more completely the elements in a metallic ore are utilized, the fewer the waste residues that will be discharged to pose a possible menace to the environment.

China, as the largest developing country and home for one-fifth of humanity, has become increasingly aware of the need for science-based approaches to sustainable development, and is chosen as the scenario. Mineral resources, which are irreplaceable and nonrenewable, on the one hand, and biomass as an everlasting resource, on the other, are used as examples in the present presentation.

This presentation first describes the so-called green technologies, targeted at reduced, and ultimately zero, pollutant effluents. Then it enumerates, as examples, processes with enhanced utilization and recovery of useful metals from low-grade and complex ores. Finally, it describes the flash pyrolysis of coal to recover the higher-value liquid hydrocarbons it contains in a manner analogous to topping for petroleum crude, instead of burning coal *ad hoc* as fuel, and it also describes small nonsmoking coal burners in which the hot combustion gas is diverted away from pyrolyzing the incoming coal feed, as well as burners in which the overall combustion reactions are decoupled, in order to reduce nitrogen oxide formation more effectively.

1. Introduction

Two significant roles that chemistry can play in life support systems and sustainable development are (1) conservation in resource utilization and (2) the preservation and control of the environment. These two roles are often interconnected. For instance, the more completely the elements in a metallic ore are utilized, the fewer the waste residues that will be discharged to pose possible menace to the environment. Conservation of resources and control of environment are not only problems for developed countries possessed with the ability to process resources and suppress pollution. In the new millennium, the developing countries will continue to play major roles as providers of resources for humanity and, in doing so, will continue to be faced with the dilemma as to what to do with the harm, actual or potential, derived from what is left after due exploitation of their resources. China, as the largest developing country and home for one-fifth of humanity, has become increasingly aware of the need for science-based approaches to sustainable development, and will therefore be chosen as the scenario. And mineral resources, which are irreplaceable and nonrenewable on the one hand, and biomass as an everlasting resource as long as the sun shines, on the other, will be used as examples in the following presentation.

2. Chemistry Basis for Zero Pollutant Effluents

Most of the existing chemical plants originated from the single concept of manufacturing certain products, relegating environmental issues to subordinate significance. To meet the growing stringent requirements for environmental protection, however, the existing plants need revamping and refurbishment for which auxiliary downstream processing units have to be added. This section will discuss, as an alternate strategy, the *chemistry basis for zero pollutant effluents* as the paradigm for future chemical process design.

Nevertheless, the goal of zero pollutant effluents cannot be realized in practice, unless a tremendous amount of research and development (R&D) work is carried out based on the principle of green processes. Processes, better than the conventional and designed

with the objective of *lower* pollutant effluents up to *zero*, are generally known as *green*. Criteria for a green process consist of the following:

- The air and water discharged from the plant should have the same or even better quality than when they enter the plant.
- No poisonous chemicals are used or generated in the plant.
- High-percentage conversion of atoms in the starting materials into products.
- High rate of reaction with no side reactions and consecutive reactions generating pollutants or wastes.
- Minimum consumption of energy and natural resources, minimum waste generation, and process ecologically satisfactory.

Three examples of green process technology will be discussed, and then the potential of utilizing biomass, an everlasting resource as long as the sun shines, will be described.

2.1. Leaching of Chromium from Iron Chromite Ores with Fused Sodium Hydroxide

Chromium compounds are important raw materials for the leather, electroplating, and metallurgical industries. Conventionally, chromium compounds are produced from the decomposition of iron chromite ore $FeO.Cr_2O_3$ and typically have the composition shown in Table 1.

| Composition	SiO_2	Al_2O_3	Cr_2O_3	FeO	CaO	MgO	TiO_2
%	6.75	12.29	47.21	23.39	1.40	9.67	0.225

Table 1. Conventionally, chromium compounds.

Iron chromite ore is traditionally roasted in a furnace at about 1150 °C with the addition of sodium carbonate leading to the following reaction:

$$2FeO \cdot Cr_2O_3 + 4Na_2CO_3 + 3.5O_2 \rightarrow Fe_2O_3 + 4Na_2CrO_4 + 4CO_2$$
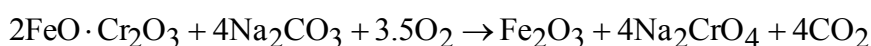
The calcine is then leached to recover chromium as Na_2CrO_4. Toxic chromium compounds, mostly hexavalent, are present in the calcine, fume, gas and the slag after leaching. The chromium left in the slag is about 5%. A large portion of the slag is recycled into the furnace as diluent and the remainder is difficult to utilize despite its still high chromium content. The storage of the slag without strict protection often leads to leakage of the soluble hexavalent chromium into the environment.

A new process has been developed by oxidizing the chromium in the iron chromite ore by air into sodium chromate in fused sodium hydroxide in a three-phase air-lift loop reactor at 500–550 °C through the following reaction:

$$2FeO \cdot Cr_2O_3 + 8NaOH + 3.5O_2 \rightarrow Fe_2O_3 + 4Na_2CrO_4 + 4H_2O$$
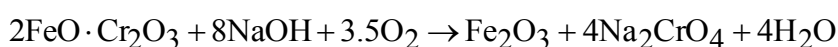
The conversion of chromium into chromate can be as high as over 99%. The difficulty of the process involves the separation and recovery of chromium from the reaction

mixture. In the proposed process, shown in Figure 1, the fused mixture is diluted with a lean recycle sodium hydroxide solution to an extent and at a temperature as determined from a specially developed phase diagram. The solid residue containing iron and magnesium is first separated from the sodium hydroxide solution, which contains chromium and aluminum. Then crude sodium chromate, containing some aluminum, is crystallized from the solution upon further dilution and cooling. By still further dilution and temperature adjustment, the aluminum left in the solution is separated as aluminum hydroxide. Table 2 compares the new process with the conventional method in terms of chromium recovery and materials consumption.

Process	New	Conventional
% of chromium recovery	>95	76
Cr slag or residue, t/t chromate	0.6	2.5
Total Cr in slag or residue, %	0.5	3.0
H_2O-soluble Cr in residue, kg/t chromate	1	17
Ore consumption, t/t chromate	1.07	1.35
Alkali consumption, t/t chromate	0.4 (NaOH)	1.0 (Na_2CO_3)
Fuel oil used, t/t chromate	0.7	0.9

Table 2. Comparison of the new process with the conventional method in terms of chromium recovery and materials consumption.
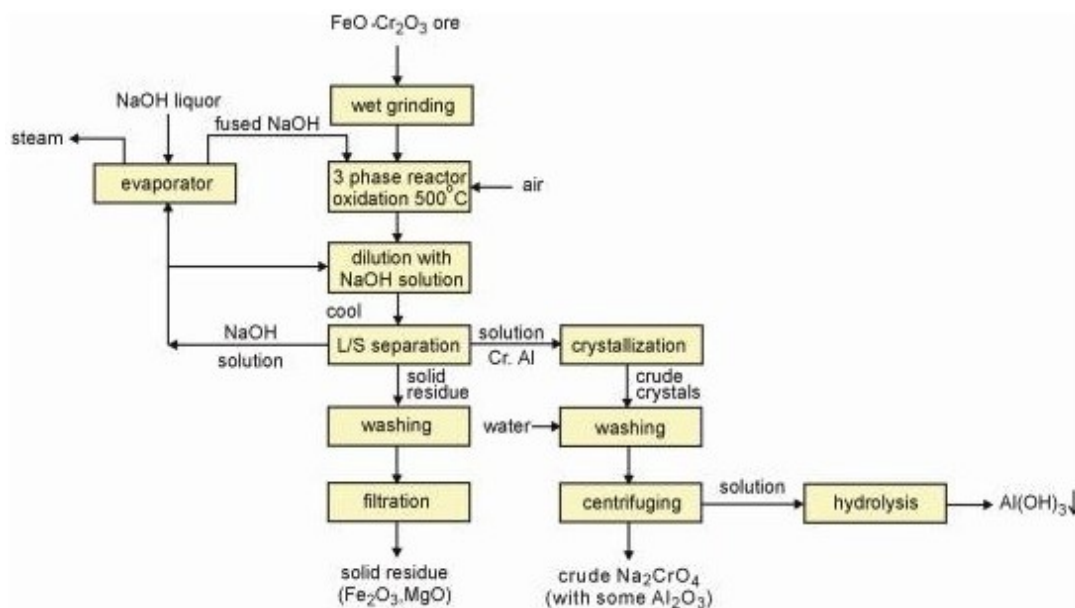
Figure 1. Schematic flowsheet of the proposed new process for chromate production (recycling of dilute sodium hydroxide solution within the process is not shown).

2.2. Extracting Lead Using a Green Process

Metallic lead is extracted conventionally by pyrometallurgical processes from ores or concentrates containing galena (PbS) by first sintering and then smelting the sinter in a shaft furnace, generating, during processing, sulfur oxides and lead-containing fumes

and dusts. A new hydrometallurgical process, as shown in Figure 2, has been developed to convert lead sulfide into lead carbonate by reacting galena in ammonium carbonate solution at 50–80 °C as follows:

$$PbS + (NH_4)_2\, CO_3 + 0.5O_2 + H_2O \rightarrow PbCO_3 + S + 2NH_4OH$$
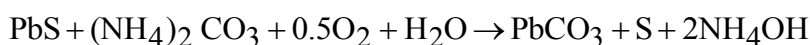
More than 80% of the sulfur in galena is converted into elemental sulfur, with the rest being oxidized into sulfur oxyacid ions in the solution. The iron sulfides in the ore were found to catalyze the conversion of galena. If the lead ore contains no iron sulfides, small amounts of FeS_2 or FeS_{1+x} can be added to increase the reaction rate. Sodium carbonate can be used instead of ammonium carbonate, leading to the formation of sodium sulfate as the oxidation product of the sulfides. After conversion, the reaction mixture can be separated by filtration. The solid residue is separated by flotation into a sulfur concentrate containing gold, silver and unreacted copper and zinc sulfides, and a tailing consisting mainly of lead carbonate, which can be further processed to lead chemicals and also to metallic lead by electrowinning.

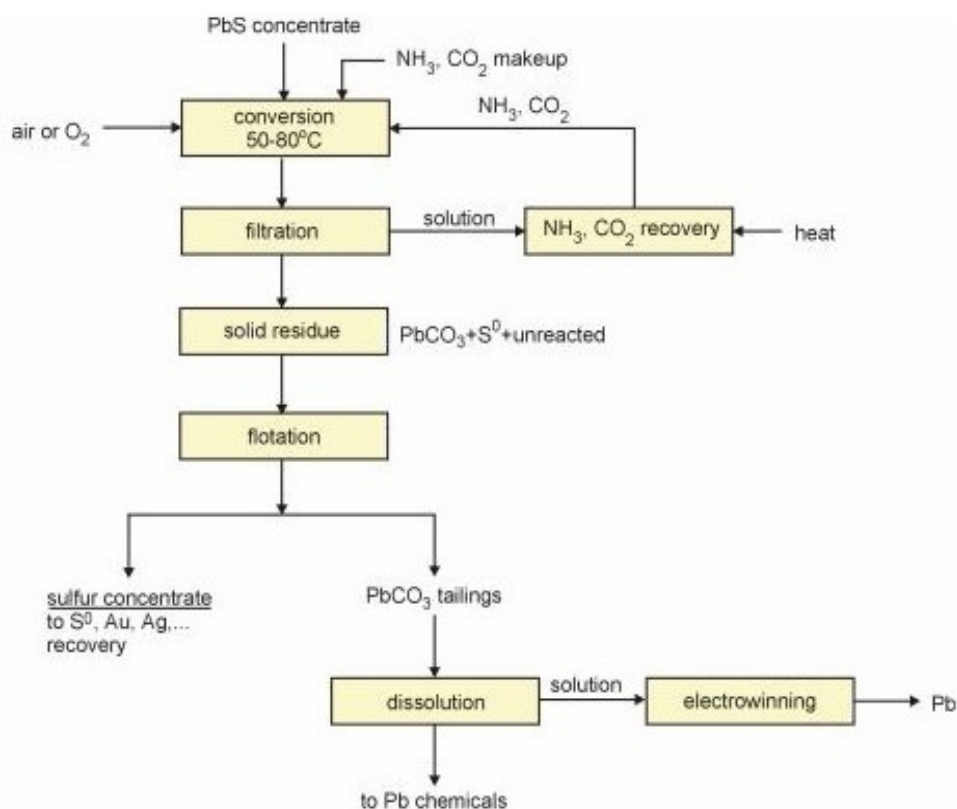Figure 2. Schematic flowsheet of lead hydrometallurgy based on the conversion of galena to lead carbonate.

In China, there are several large deposits of galena containing gold. While ordinary gold ore processors would only accept ores containing <1% Pb, our hydrometallurgical process can be used to treat concentrates in a first step for converting more than 88% of the lead into carbonate, as shown in Table 3.

Sample	Pb (%)	Cu (%)	Fe (%)	Ni (%)	S (%)	CaO (%)	SiO$_2$ (%)	Au (g L^{-1})	Ag (g L^{-1})
1	40.8	3.08	16.9	0.05	22.9	0.47	7.10	68.6	476.9
2	37.4	2.38	12.6	0.06	17.8	0.33	20.6	71.3	328.0
3	43.0	2.34	15.4	0.04	18.9	0.59	5.86	44.5	347.8

Table 3. Hydrometallurgical process can be used to treat concentrates in a first step for converting more than 88% of the lead into carbonate.

	Au (gt^{-1})	Ag (g t^{-1})	Cu (%)	Pb (%)	Fe (%)	CaO (%)	SiO$_2$ (%)	S (%)	C (%)
Concentrate	98.2	869.6	6.93	3.66	41.0	0.06	0.20	36.8	0.34
Tailing	26.0	163.5	0.93	52.5	8.87	0.30	6.64	2.80	3.14

Table 4. Lists of the separation of lead, gold as well as other elements by the proposed process, after separation of the solid reaction mixture by single-stage foam flotation

## 2.3. Leaching of Gold Ore with Thiosulfate

Conventionally, gold is extracted from oxidized ores by leaching with sodium cyanide solution followed by adsorption with activated carbon. Not only is the pollution problem hard to deal with, but ores containing sulfur, arsenic or/and carbon have to be first treated by either high temperature roasting, high pressure aqueous oxidation or bacteria pre-leaching, in order to free or expose the gold particles to the cyanide solution in the succeeding step of leaching.

Thiosulfate leaching has been investigated for recovering gold from sulfide concentrates having the typical compositions shown in Table 5, in which gold is mainly finely dispersed in pyrite and chalcopyrite.

Sample	SiO$_2$ (%)	Al$_2$O$_3$ (%)	Fe$_2$O$_3$ (%)	CaO (%)	MgO (%)	MnO (%)	S (%)	Cu (%)	Ag (g t^{-1})	Au (g t^{-1})
A	37.95	5.75	28.9	0.39	0.28	0.048	20.59	3.19	60.0	50.4
B	32.84	3.41	38.17	1.06	0.42	0.113	31.37	0.018	36.0	92.8

Table 5. Thiosulfate leaching has been investigated for recovering gold from sulfide concentrates having the following typical compositions, in which gold is mainly finely dispersed in pyrite and chalcopyrite,:

The gangue consists mainly of quartz and calcite. The reaction of leaching of gold can be represented as follows:
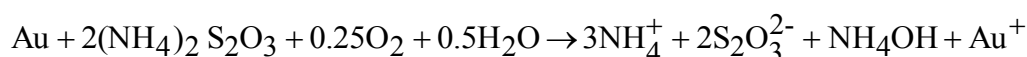
$$Au + 2(NH_4)_2 S_2O_3 + 0.25O_2 + 0.5H_2O \rightarrow 3NH_4^+ + 2S_2O_3^{2-} + NH_4OH + Au^+$$

Results of leaching gold from sample A, at 50 °C for 1.5 hours with a solid/liquid ratio of 1/3 m^3.t, are shown in Table 6.

Solution composition (mol dm^{-3})				% extraction		
Na$_2$S$_2$O$_3$	NH$_4$OH	(NH$_4$)$_2$SO$_4$	Cu (g dm^{-3})	Au	Ag	Cu
0.5	2.0	0.2	2.0	95.5	51.3	16.8
0.7	2.0	0.2	2.0	95.9	55.9	13.5
1.0	2.0	0.2	2.0	95.1	57.5	12.7
0.7	2.0	0.1	2.0	95.9	60.0	15.7
0.7	2.0	0.4	2.0	95.1	54.9	11.9

Table 6. Results of leaching gold from sample A, at 50°C for 1.5 hours with a solid/liquid ratio of 1/3 m^3.t, are shown as follows:

The concentrate has to be finely ground up to about 80% <200 mesh. The poor extraction of silver needs further study. The cupric ammonia complex catalyzes the leaching reaction and the addition of ammonia also prevents the precipitation of copper sulfide. Ammonium sulfite or sulfate is added to minimize the decomposition of the thiosulfate.

Further proposed has been the use of elemental sulfur through phase transfer catalysis by disproportionation reaction to form thiosulfate and polysulfides. The reaction solution is then oxidized by bubbling air at 50°C to oxidize the polysulfides in solution into thiosulfate and some other oxyacids, and the solution can then be used for gold leaching. The reaction can be expressed by:

$$2(x+1)\text{S} + 6\text{OH}^- \rightarrow \text{S}_2\text{O}_3^{2\text{-}} + 2\text{S}_x^{2\text{-}} + 3\text{H}_2\text{O}$$

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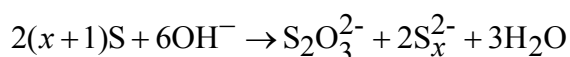
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Biographical Sketches

Mooson Kwauk (Guo Musun) was born in 1920, in Hangyang. He obtained his BS in chemistry from the University of Shanghai in 1943; and an MS, in Chemical Engineering, from Princeton University in 1946. He became a professor in 1956 and director in 1978 of the Institute of Chemical Metallurgy, Chinese Academy of Sciences, Beijing; in 1986 he became director emeritus. His publications include: Fluid-Bed Technology for Extractive Metallurgy, 1958; Fluidization: Dynamics of Uniform Spherical Particles and Fluid in Vertical Systems, 1963; Fluidized Leaching and Washing, 1979; Fluidization: Idealized and Bubbleless, 1992; Fast Fluidization, 1994; Particle-Fluid Two-Phase Flow—the Energy-Minimization Multi-Scale Method, 1994; Geometric Mobiles, 1998. He has been a member of the Chines Academy of Sciences since 1980.

Jiayong Chen was born 1922, in Sichuan Province, China. He obtained a BS in chemical engineering from the National Central University, Chungking, China, in 1943; MS in 1949, and Ph.D. in 1951, from the University of Illinois at Urbana-Champaign. Since 1956 he has been a professor at the Institute of Chemical Metallurgy, Chinese Academy of Sciences, Beijing. Publications include: Separation and Utilization of Iron in Hydrometallurgy, 1991; Principles of Transport Phenomena, 1997; Hydrometallurgy Research and Development, 1998; and over 160 papers in chemical engineering and chemical technology. He has been a member of the Chinese Academy of Sciences since 1980.

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Jinghai Li was born in 1956, in Shanxi, China. He obtained his BS and MS in thermoenergy, from Harbin Institute of Technology, in 1982 and 1984, respectively, and a Ph.D. from the Institute of Chemical Metallurgy in 1987. Since 1993 he has been a professor at the Institute of Chemical Metallurgy, Chinese Academy of Sciences, Beijing. He has published 124 papers, 11 patents, and one monograph: Particle-Fluid Two-Phase Flow—Energy- Minimization Multi-Scale Method, Beijing, 1994.

Qingshi Zhu was born in 1946 in Chengdu, Sichuan Province, China. In 1968 he graduated from the Department of Modern Physics, University of Science and Technology of China. He is now a professor and president of the University of Science and Technology of China in Heifei. Other appointments include: director of Laser Chemistry Division, Qinghai Institute of Salt Lake; and director of Laser Chemistry Division, Dalian Institute of Chemical Physics. He has published 120 scientific papers

including: Progress in Green Chemistry (1997); Green Chemistry and Sustainable Development (1997); Greenization of Chemistry and Chemical Transformation of Green Plants (1998); Liquid Phase Nanochemistry (with Li Ming-zhangshi; 1998). He has been a member of the Chines Academy of Sciences since 1991.