cess controllers. A more recent introduction is the Type EQ, a high-performance temperature transmitter that accepts single/dual RTD-, thermocouple- or mV-inputs; the output is a 4-20-mA signal with a repeatability of 0.05% of input span.

Bailey's transmitters can send messages — e.g., their identity and configuration, and whether they're operating properly — but not process information in a digital form. Messages are transmitted as digital pulses superimposed on the 4-20-mA analog output representing the process measurement. The data can be sent to the firm's System 90 process controller or its handheld terminal, the STT01, or to a personal computer (including the IBM-PC).

Reverse communication (from controller to transmitter) is done by slightly changing the line voltage. According to Bailey, the duration and magnitude of the messages (to and from) take up such a small percentage of the transmitter's total output that this does not significantly affect the unit's operation.

According to John Blagrave, senior product marketing manager, a new all-digital system similar to Honeywell's will be introduced by midyear. With this in mind, the firm has recently upgraded the electronics of the BC transmitters to enable them to send both process information and messages digitally. EQ units also will have digital capability.

The Sensor-Mate 4500, a temperature transmitter from Weed Instrument (Austin, Tex.), works on a principle similar to that of Bailey's message-sending units. In this case, a Hewlett-Packard HP-94 calculator is used as a handheld terminal. The HP-94 plugs directly into any termination point in the 2-wire line connecting the transmitter to the main process controller.

The calculator sends messages as a low-voltage signal on top of the transmitter's analog signal. During message transmission, the value of the analog output is distorted by about 4%. However, says the firm, such distortions last for only about five seconds, since the HP-94 transfers data at a fairly fast rate of 2,400 baud (words/min.).

Jayadev Chowdhury

Recyclers try new ways to process spent catalysts

Because of the decline in metal prices, processors working with base-metal materials are having to come up with more-efficient and economic metal-reclamation routes.

Those concerned with the disposal of spent base-metal catalysts are in a dither these days. On one hand, environmental regulations are making it more difficult to put the waste material in landfills. On the other, low metal prices have put the squeeze on companies that process spent catalysts to recover the metals. Thus, the recyclers are busy working on innovations that might do the job more efficiently and economically. (The situation is different for precious-metal catalysts, which are processed for the metals' intrinsic value [see box].)

Estimates of the volume of spent base-metal catalyst available for recycling vary. Lori Feldman, general manager of Catalyst Disposal Services (Canada) Ltd. (Calgary, Alta.), says that the annual tonnage in the U.S. and Canada could be as high as 50,000 tons, of which roughly one-fifth would be heavy metals (i.e., excluding the substrate). This number roughly jibes with a study done for the U.S. Bureau of Mines about four years ago, which calculated the annual metals content in the U.S. at approximately 27 million lb (13,500 tons). The volume is probably smaller now because of the dropoff in U.S. crude-oil refining, says Frank Hennion, coauthor of the study, who recently retired as resource manager of Inmetco (Ellwood City, Pa.). More than half of the tonnage consists of hydrodesulfurization catalysts, say industry spokesmen.

ARE THEY HAZARDOUS? — While the catalysts themselves may not necessarily be hazardous, their contamination from processing often makes it questionable whether they can meet U.S. Environmental Protection Agency or state regulations. The EPA criteria are: ignitability (flash point less than 140°F); corrosivity (pH less than 2 or greater than 12.5) or other corrosivity standards; reactivity; and extraction-procedure toxicity — i.e., the ability of toxic

Texasgulf Minerals and Metals, Inc.

Workers tap platinum-iron alloy from a plasma electric-arc furnace compounds to leach from waste at rates exceeding EPA limits. (EPA is expected to add nickel to its hazardous-waste list.)

"The problem is that test procedures covering these criteria have not been fully specified," says Mark Neal, catalyst development coordinator with Exxon Research and Development Laboratories (Baton Rouge, La.). "So some refiners are just playing it safe and declaring their material hazardous." Neal notes that recycling is the ideal way to dispose of spent catalyst because it's costly to put it in landfills "and you never get rid of the liability for it."

RECOVERY METHODS — Gulf Chemical & Metallurgical Corp., which claims to be the world's largest recycler of spent hydroprocessing catalysts, has been recovering molybdenum and vanadium from cobalt-molybdenum and nickel-molybdenum catalysts for many years. Current capacity at the firm's Freeport, Tex., plant is about 30,000 tons/yr, says general manager William Deering, but a new roaster, scheduled to go onstream this year, will increase this to about 40,000 tons/yr.

In Gulf's process, molybdenum and vanadium are converted to their sodium salts by adding sodium carbonate during a multiple-hearth roast at 650-900°C (the temperature depends on the catalyst feed). The roast also removes carbon and sulfur. Calcined material is quenched in water, which dissolves the salts. Then the leach liquor is separated from the insolubles by countercurrent decantation.

Ammonium chloride is added to precipitate ammonium vanadate, which is calcined and fused to produce vanadium pentoxide. The remaining solution is then heated to 80-85°C and acidified to precipitate molybdic acid, which is calcined to molybdic oxide. Gulf claims that molybdenum and vanadium recovery can reach 98%.

The company has about 150,000 tons of stockpiled cobalt- and nickel-bearing material that it hasn't been able to process economically because each metal is only a minor catalyst component (1.5-2%). One particular problem is that in the roast this material forms spinels (stable compounds difficult to dissociate) with the alumina.

A pyrometallurgical route to recover cobalt and nickel alloys from these tailings has been piloted in Ghent, Belgium, by Sadacem (both Sadacem and Gulf are owned by Société Générale de Belgique). The firm is modifying some of its existing pyrometallurgical facilities to start handling Gulf's tailings this year, says Deering.

CRI-MET, a partnership of AMAX Inc. (Greenwich, Conn.) and CRIV (Baltimore, Md.), feels that its caustic process, which recovers all the metals from hydrotreating catalysts (including the alumina substrate), is a complete answer to the recycling problem. (CRIV is a joint venture of CRI International Inc., Baltimore, and Shell Chemical Co., Houston.) CRI-MET's plant, which went onstream last summer at the AMAX Port Nickel plant near New Orleans, has an annual capacity of around 30,000 tons/yr.

"Our plant is environmentally clean," says William Bilhorn, vice-president of AMAX's metals group. "Everything that goes in comes out as a salable product, and there are no residues." He adds that a particular economic advantage is that the process uses some equipment formerly employed by the nickel plant, which has been idle since the fall of 1985.

In the AMAX process, ground, alumina-based catalyst is subjected to two caustic leaches, each done at around

Catalysts as a source of precious metals

Recovery of precious metals — mainly platinum-group ones — from spent catalysts is a well-established business because of the metals' high value.

One basic procedure is to smelt the spent material and accumulate the desired products on collector metals — e.g., iron or copper. Then the collector is acid-leached. With alumina-based catalysts (reforming catalysts or automobile catalytic-converter pellets), the alumina may be dissolved first by an acid leach — sulfuric acid if an alum product is desired, or hydrochloric acid for aluminum chloride. Carbon substrates are removed by incineration.

Residue containing the precious metals then goes through a series of hydrometallurgical steps for recovery. PGP Industries, Inc. (Santa Fe Springs, Calif.), which processes spent catalysts used in pharmaceutical and intermediate-chemicals production, dissolves the residue in hydrochloric acid with an oxidant — e.g., nitric acid. "Acid alone won't work with precious metals except silver," explains Robert Henning, vice-president, manufacturing.

PGP recovers platinum, palladium, rhodium, iridium, ruthenium, rhenium, gold and silver. Typically, platinum or palladium are removed first. Platinum is precipitated as ammonium platinate by adding ammonium chloride. This is redissolved, base-metal and precious-metal contaminants are removed by hydrolysis and filtration, then 99.95%-pure platinum sponge is obtained from the purified solution.

High yields as well as high purity are critical, says Henning. "If you operated with only 95% recovery, you'd be out of business because of the cost of the metal," he explains. "We get yields in the high 90s, first pass, depending on the metal, but there is a lot of treatment of residual streams."

While processors generally use known techniques, they guard their knowhow. "Basically, it's a question of combining various technologies and doing some innovation to do a job efficiently," says M. I. El Guindy, vice-president and chief operating officer of Gemini Industries Inc. (Santa Ana, Calif.). "It's like making chile."

Gemini used to process spent auto-catalysts, but now 95% of its business is in reforming catalysts. The company claims to be number one in that business, with a capacity of 3 million lb/h per shift. El Guindy estimates the U.S. market for platinum-group metals obtained from spent reforming catalysts at less than 6 million lb/yr.

"We got out of auto catalysts because of the problems of collecting the material," he says. He notes that alumina-based auto-catalyst pellets are processed like reforming catalysts, but have an average loading of only about 300 ppm platinum and 100 ppm palladium, while the honeycomb type (a ceramic base with an alumina coating) has about 800 ppm platinum and 300 ppm palladium. The honeycomb must be broken up and the metals leached or smelted from the base. (In contrast, reforming catalysts average about 3,000 ppm platinum.)

A leading company in auto-catalyst recycling is Texasgulf Minerals and Metals, Inc. (Anniston, Ala.), which uses a plasma smelting process developed by Tetronics Research & Development P/L (Faringdon, England). Texasgulf has a worldwide exclusive license to use the route for platinum-group metals, says James Saville, vice-president of Texasgulf's plasma smelting division.

He notes that a basic advantage of the plasma technique is that the temperature and stirring conditions of the melt can be carefully controlled, whereas a submerged-arc furnace does not allow this control (there is vigorous stirring). Says Saville: "If you stir too rapidly, you won't get the platinum to settle out." The furnace operates at around 1,500-1,600°C. Alumina melts at about 2,050°C, but Saville notes that lime is mixed with alumina-based pellets to reduce the melting point. Platinum recovery is said to be more than 90%.

Texasgulf ships concentrate to Johnson Matthey Inc. (West Deptford, N.J.) for refining. Johnson Matthey processes platinum-group metals, and has its own smelting and hydrometallurgical operations.

In Japan, Nippon Engelhard Ltd. (Tokyo) is believed to be the leader in recycling spent auto-catalysts. The company uses both dry and wet smelting to recover eight precious metals, and has an annual recovery capacity of: 5,000 kg each for palladium, gold and silver; 1,500 kg for platinum; 1,000 kg for ruthenium; 800 kg for rhodium; 400 kg for rhenium; and 200 kg for iridium.

European cars are just beginning to use catalytic converters. Comptoir Lyon Alemand Louyot (Paris), France's biggest precious-metals company, reports that the volume of spent catalyst has dropped in recent years because of refinery closures and increased use of continuously regenerated reforming processes.

In Germany, Degussa says it has developed three processes that can separate platinum, palladium and rhodium from conventional U.S.-made catalytic converters. The company is in touch with German automakers, and is working on plans to collect spent converters in the future.

300°F or more and 300-500 psig. The first is a weak sodium hydroxide leach that extracts molybdenum and vanadium metal.

Residue is filtered from the solution, then molybdenum is precipitated as molybdenum trisulfide by adding sulfuric acid, and sparging hydrogen sulfide gas under pressure. Vanadium pentoxide (with applications in the steel industry) is precipitated by adding an alkali (sodium hydroxide).

The second, stronger, sodium hydroxide leach extracts alumina, which is precipitated as alumina trihydrate, a salable product, by reducing the temperature to 140-190°F. The residue, containing cobalt and nickel, is sold as is for refining, says Bilhorn.

An important question is whether there is sufficient material available to keep both the Gulf and CRI-MET plants running economically. Russell Goerlich, general manager of CRI-MET, speculates that there is roughly as much hydrotreating catalyst available in the rest of the world as in the U.S. (Bilhorn claims that the CRI-MET plant was operating above 80% capacity at yearend.)

RECOVERY ELSEWHERE — Metals recovery from spent catalysts is flourishing outside the U.S. In Japan, the Spent Catalyst Recovery Assn. (Tokyo), which claims to be the only trade group of its kind in the world, has 35 corporate members. Many are nonferrous-metals producers, and a number specialize in precious metals.

Taiyo Mining and Industrial Co. (Kobe), a ferroalloys producer, has a plant capable of treating 6,000 metric tons/yr of spent catalysts to recover molybdenum, vanadium, niobium, nickel and cobalt, while Catalysts and Chemical Industries Co., a joint venture of JGC Corp. and Asahi Glass Co. (all of Tokyo) runs a 40-metric-ton/mo plant for bismuth and molybdenum recovery.

Full Yield Industries (Miao-Li, Taiwan) has operated a plant for spent hydrotreating catalysts for several years. The process leaves no residue, says Regis Lippert, president of Intercat Inc. (Sea Girt, N.J.), whose company ships waste catalyst to Taiwan. The Full Yield technique uses a roast to burn off hydrocarbons, followed by caustic leaching for the metals, he notes. France's Européenne de Retraitement de Catalyseurs (Eurecat, La Voulte-sur-Rhône) uses a variety of techniques (*Chem. Eng.*, Jan. 19, p. 11) — depending on impurities contained in the feed — for recovering molybdenum, nickel, vanadium, cobalt and some tungsten from spent hydrotreating catalysts. Eurecat's facilities include a 1,000°C-plus furnace; acid and alkali chemical treatment units; and extractive distillation, evaporation and ion-exchange equipment. In addition, the company claims to be the biggest independent hydrotreating-catalyst regenerator in Europe.

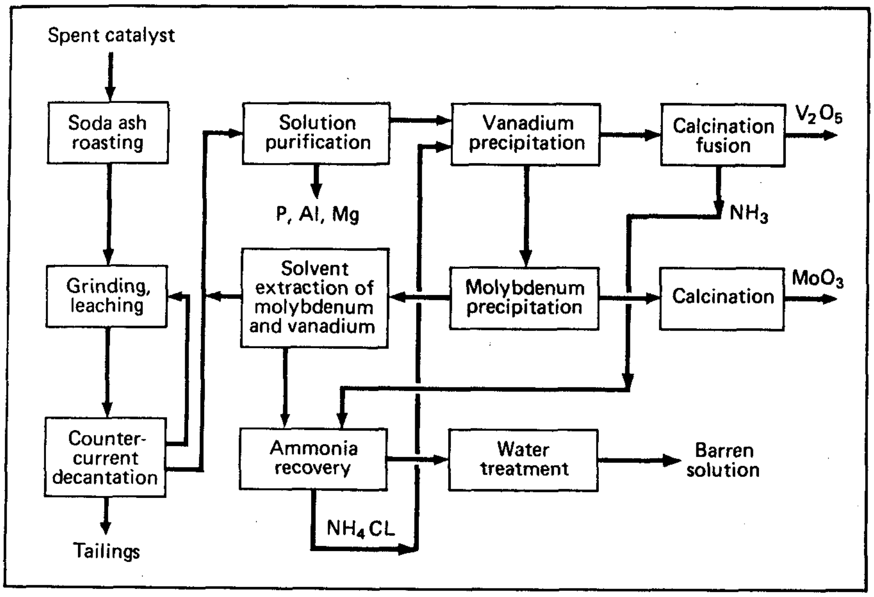
OTHER TECHNIQUES — The startup of the CRI-MET plant has put a crimp in the catalyst-processing plans of some North American companies. The Hall Chemical Co. (Wickliffe, Ohio), for example, has completed development of an acid process for hydrotreating catalysts, but is still considering the economics of a commercial plant. Hall, which sells metallic salts to catalyst manufacturers, has piloted the process at about 500 lb/d at its Arab, Ala., facilities.

"We recover about 98% of the materials as individual products," says Carl Cross, vice-president of sales and marketing. "If you don't do that, the economics are not very good. The sequence of recovery is what's unique, and this is important in getting that level of recovery."

Hall dissolves everything in hydrochloric acid, then molybdenum is precipitated first, as a sulfide, by adding H_2S. Next, vanadium is taken out by solvent extraction, reclaimed by adding caustic soda, and precipitated as vanadium pentoxide. Nickel is removed by solvent extraction, then recovered as a sulfate by adding sulfuric acid. Cobalt is salvaged in a similar manner. Tungsten recovery would be similar to that of molybdenum, says Cross, but tungsten-bearing catalysts would not be mixed with the other metals because the precipitation conditions are almost identical to those of molybdenum.

The U.S. Bureau of Mines' Albany, Ore., research center has done laboratory-scale tests of chlorination, hydrometallurgical and pyrometallurgical methods to recover nickel, molybdenum, tungsten, copper and chromium from spent catalysts. Testing ended at the end of September, says David Nelson, a group supervisor, and an economic evaluation is almost finished. In the tests, chlorination was usually preceded by a 400°C roast to remove sulfur and moisture, then spent catalysts were chlorinated at 450°C for 30 min in a nitrogen-fluidized bed. More than 80% of the Ni, Mo, W and Cu was extracted from most materials evaluated, according to the Bureau. However, only 73% of the Ni and less than 5% of the Al were reclaimed from a Ni-W-Al catalyst.

A sodium hydroxide leach extracted more than 90% W and Mo, but was poor for Al, while sulfuric acid removed more than 90% of the Ni, Mo and Cu. A sodium carbonate roast, followed by water leaching, extracted more than 90% of the Mo or Cr and 77% of W, while sodium hydroxide roasting showed promise for a Cr-Fe catalyst, says researcher B. W. Jong.



Gulf Chemical & Metallurgical Corp.

Process recovers molybdenum and vanadium from spent catalysts

Chevron Research Co. (Richmond, Calif.) has piloted a leach process in which spent catalyst is roasted, then subjected to an ammoniacal leach that dissolves everything but the alumina substrate. "We control the roast carefully, so that we don't produce spinel compounds that are difficult to leach," says Gale Hubred, leader of the environmental and mineral process development group. "This allows us to leach under mild conditions. An aggressive leach would also dissolve the alumina, and complicate the separations."

Alumina is filtered from the solution, and could be melted to make abrasives, he adds. Molybdenum and vanadium are co-extracted with a commercial solvent and co-stripped by a proprietary method. The former is further solvent-extracted, stripped and calcined to obtain molybdenum trioxide. Nickel and then cobalt are solvent-extracted and stripped with acid or ammonia to yield metal salts.

Chevron wants to license the process, and is talking with potential clients, says Hubred, noting that: "We feel our method is about the most economical available for a new facility, because we attack only the metals of value, and recover catalyst-grade metal salts."

RECYCLING OTHER CATALYSTS — While hydrotreating catalysts appear to be the most recyclable among the base-metal materials because of their volume and metal values, various companies are recycling other types.

Inmetco, whose principal business is reclamation of flue dust, mill scale and swarf from the steel industry, recovers nickel-bearing and fixed-bed catalysts used in gas reforming and ammonia plants. The material is blended with the feed to Inmetco's roaster-smelter process, which produces ferronickel chrome-alloy pig for the steel industry. The company also handles Raney nickel and activated-nickel catalysts.

Catalyst Disposal Services (Calgary, Alta.) does not process spent catalysts, but passes the materials on to various industries that are able to use them in their processes, says the company's Lori Feldman. The key is finding users, he adds. Having brokered about 7,000 tons last year, Feldman notes he will accept anything but precious-metal catalysts.

He hopes to broaden his business through a hydrometallurgical reclamation process being developed for the company by the Ontario Research Foundation (Mississauga). The route is still in the research stage, but Feldman claims it has recovered up to 99% of the available cobalt, nickel, molybdenum and tungsten from spent catalysts.

Meanwhile, in Edmonton, Alta., Vadnore Enterprises Ltd. is awaiting a delayed expansion of Syncrude Canada Ltd.'s production that could provide an adequate feed supply for a technique to recover vanadium from spent catalyst or flyash. "The process is a variation of one developed by the University of Alberta, and is tailored to tar sand residues, which contain a lot of vanadium," says company president William Middagh. Catalyst or flyash is roasted with sodium chloride, forming sodium vanadate and sodium molybdate, which are water soluble. Vanadium is precipitated as ammonium vanadate by adding ammonia, then decomposed to vanadium pentoxide by heating. Molybdenum is precipitated as calcium molybdate by adding calcium.

Biotechnology may also find a niche in the field. Hazen Research Inc. (Golden, Colo.) and Bio-Technical Resources Inc. (Manitowoc, Wis.) have formed a joint venture, Biomet Inc. (Golden), that is in the early stages of research on a microbial method of removing metals from the substrate. A potential advantage, say the companies, is that the substrate may be left intact and available for reuse.

Gerald Parkinson. McGraw-Hill World News contributors: **Shota Ushio** (Tokyo), **Mark Hibbs** (Bonn), and **David Hunter** (Paris)

Du Pont sues over polyester resins

Du Pont Co. (Wilmington, Del.) has charged Allied-Signal Inc. (Morristown, N.J.) with patent infringement relating to thermoplastic polyester resins, in a suit filed in the U.S. District Court at Wilmington. The plaintiff is asking for an injunction to prevent Allied-Signal from continuing this alleged infringement, and is seeking damages for past violations.

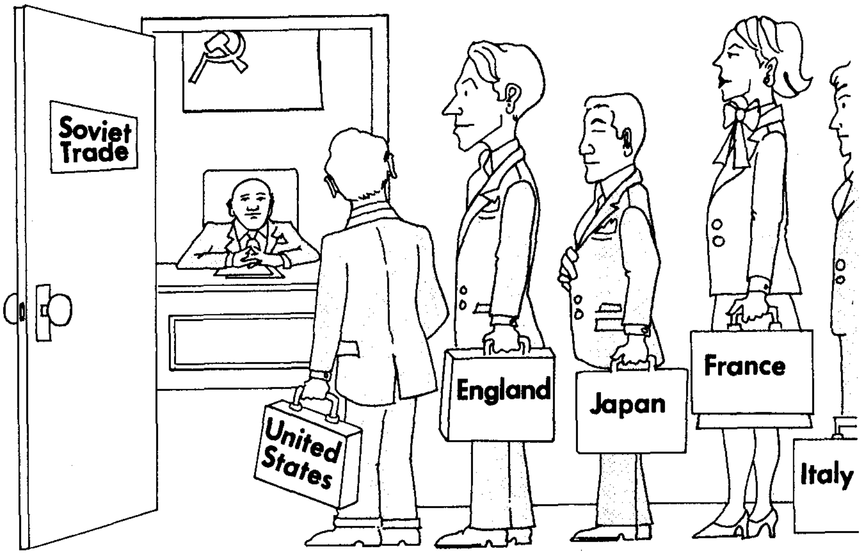
Du Pont introduced its Rynite polyester thermoplastic in 1978; the compound is used in engineering components. The firm states that a product made by Allied-Signal, under the trademark Petra, violates its patent.

The Du Pont patent, says a spokesman, is the result of many years of research and financial investment to develop resins with improved moldability. The technology has resulted in more than 20 different types of Rynite, used in applications previously served by various other materials.

"Du Pont has invested millions of dollars in this technology to reduce costs for its customers and increase benefits for consumers," says Lawrence H. Gillespie Jr., a director at the firm's Polymer Products Dept. "We intend to protect this investment under the rights granted us by the U.S. patent system."

Soviets ready to team up with Western CPI partners

Gorbachev is bent on liberalizing the nation's trade and investment policy, and has asked Western chemical-process-industries firms to submit joint-venture proposals.



Since Stalin's time, many multinational firms have found trading with the Soviet Union a trying experience. For years, almost all dealings with such corporations have been conducted exclusively at the Ministry of Foreign Trade in Moscow, whose pompous "wedding cake" architectural design served as an aesthetic warning of the monolithic and often infuriating trade bureaucracy within. All trade was tightly centralized. Moscow bureaucrats bought and sold as they pleased, often with little or no coordination with the factories that actually handled the goods.

But now, the Soviet Union has embarked on the most ambitious reform of foreign trade in decades. The changes are bound to create fresh opportunities for the chemical process industries, because chemicals are one of the five major economic areas targeted for expansion through increased trade.

OPENING THE DOOR — In fact, as of Jan. 1, some 20 Soviet ministries and 70 amalgamations and enterprises, including some dealing with chemicals, are allowed to conduct trade negotiations with foreign firms on their own. They will be permitted to handle hard-currency credits, and reinvest some of their trade earnings as they see fit. The plan was approved in principle by the ruling Soviet politburo last summer.

Western business firms, somewhat jaundiced by frequent past overtures and withdrawals from Soviet Union officials, nevertheless appear genuinely excited about the new setup. In early December, over 300 executives gathered in New York at the annual U.S.–U.S.S.R. Trade Council meeting. (The Council, based in New York, meets in Moscow on alternate years.)

"There were about 75 more high-level business participants this year, compared with 1984," says William Forrester, director of communications for the Council. "The changes in Soviet policy are generating a lot of interest here." Of course, U.S. companies are not the only ones interested in getting in; numerous European and Japanese firms also are reportedly pursuing negotiations.

In an even more unusual break with the past, Soviet planners are considering allowing direct foreign investment in the country for the first time. Officials are reportedly drafting new legislation outlining the setup of Soviet/for-