Table 1. Characteristics of several Ni-containing methanation catalysts.

Catalyst*	Decomposition product	Sample weight (g)	Sample area (m^2)	Surface area per mass (m^2/g)	Saturation temperature† (°C)	CH_4‡ (moles (per 100 moles)	CO_2 (moles (per 100 moles)	C_2H_6 content	H_2S‡§ (cm^3)
"$ThNi_5$"	Ni/ThO_2	0.5012	9.0	18	≥291	7.2 (209)	0.1	Small amount	78 (291)
"UNi_5"	Ni/UO_2	0.2020	6.1	30	≥367	0.7 (218)	0.03	Trace	25 (288)
"$ZrNi_5$"	Ni/ZrO_2	0.5199	14.6	28	≥362	0.7 (206)	0.004	Trace	10 (356)
Harshaw Ni		0.1630	20.4	125	≥291	3.6 (217)	0.006	Small amount	40 (285)

*Quotes signify that the enclosed is the precursor to the actual catalyst. †At the saturation temperature only insignificant amounts of CO remain unreacted. ‡The number in parentheses is the experimental temperature (in degrees Celsius). §The volume of H_2S at standard temperature and pressure needed to completely deactivate the catalyst.

drogen absorbers (*1*). Since the hydrogen is absorbed dissociatively (*2*), it must be present on the surface, at least fleetingly, as a monatomic species. For this reason it appeared that the MT_5 compounds might be effective hydrogenation catalysts. This expectation has been borne out in recent work involving the synthesis of NH_3 from the elements (*3*) and in the reaction of CO + H_2 to form CH_4 (*4*). In our earlier experiments the intermetallic compounds investigated were of the type RNi_5. In the work reported here we have considered MNi_5 intermetallics in which M represents a non-rare-earth element.

The reaction of CO + H_2 over $ThNi_5$, UNi_5, or $ZrNi_5$ was studied in a flow reactor. The molar ratio of H_2 to CO was 3:1. The quantities of catalyst used varied between 0.2 and 0.5 g. The space velocity was about 6700 $hour^{-1}$, which is sufficiently high to avoid limitation by diffusion. The activities of the MNi_5 samples (or of the decomposition products of these intermetallics) were compared at ~200°C, where the conversion is small. At this temperature the reaction is in the kinetic region, and heat and mass transfer effects are negligible. (At higher temperatures the conversion of CO is essentially complete and hence it is not possible to compare relative catalytic effectiveness.)

We analyzed the gas mixture emerging from the reactor with a gas chromatograph. Surface areas were measured in situ by the continuous flow method of Nelsen and Eggertsen (*5*). We carried out this measurement using a mixture of N_2 and He gases (25 moles of N_2 per 100 moles of the gas mixture).

The activities of the intermetallics are indicated in Table 1. Results for Harshaw Ni-0104T are included for comparison. X-ray diffraction studies of these non-rare-earth MNi_5 catalysts showed, as was the case for our earlier studies of RNi_5 catalysts, extensive decomposition into Ni and the oxide of the partner metal. As a result of our studies of RNi_5 catalysts we believed that the active species was Ni supported on the rare-earth oxide (*4*); however, the activity varied considerably among the catalysts studied. This is also true of the MNi_5 intermetallics studied in the present investigation. We believe that the difference is a consequence of variations in the Ni surface or of specific interactions between the metal and the supporting oxide, or both.

We also studied the sensitivity of the catalysts to poisoning by H_2S by injecting small volumes of H_2S gas into the reaction mixture in steps and noting the decline in catalyst activity. The quantities of H_2S needed to poison the catalysts completely are given in Table 1. Dalla Betta *et al.* studied H_2S poisoning for several Ni methanation catalysts and observed (*6*) that a continuous feed of H_2S (10 parts per million) was sufficient to significantly lower their steady-state activities. The steady-state activity of the unpoisoned catalyst is in the order Raney Ni > Ni/Al_2O_3 > Ni/ZrO_2 (where Ni/Al_2O_3 represents Ni supported on alumina), but this order reverses after poisoning. As indicated in Table 1, "$ZrNi_5$" is much more susceptible to H_2S poisoning than the other compounds, and "$ThNi_5$" is relatively resistant to H_2S. Thus the nature of the element with which Ni is combined in the precursor intermetallic compound is also important.

Although the surface area of the catalyst produced from $ThNi_5$ is relatively low, its activity as a methanation catalyst is the highest of the four systems studied. Its specific activity in yield per square meter of surface area exceeds that of the commercially available methanation catalyst (Harshaw Ni-0104T) by a factor of about 5.

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Mercury Emissions from Geothermal Power Plants

Abstract. *Geothermal steam used for power production contains significant quantities of volatile mercury. Much of this mercury escapes to the atmosphere as elemental mercury vapor in cooling tower exhausts. Mercury emissions from geothermal power plants, on a per megawatt (electric) basis, are comparable to releases from coal-fired power plants.*

Recent reports (*1–4*) have expressed concern about the potential toxicity hazards and environmental contamination of mercury emissions from geothermal areas in Hawaii, New Zealand, and Iceland. Indeed, mercury has been shown to be associated in elevated concentrations in a wide variety of natural thermal fluids (*5–8*). Natural mercury contamination of the marine environment during volcanic activity has also been reported (*9*), and other studies of mercury distributions in the oceans and their sediments strongly suggest that large quantities of mercury enter the oceans from submarine volcanic activity (*10–13*).

Because of this potential for mercury mobilization, a research program was initiated to study mercury emissions from existing geothermal power plants. We present here our initial findings of the quantities and chemical forms of mercury in emissions from two producing geothermal power developments: the

Table 1. Mercury concentrations and chemical forms in geothermal fluids.

Sample	Mercury (ng/liter)					
	Cerro Prieto, main unit	The Geysers				
		Unit 3	Unit 4	Unit 7	Unit 8	Unit 11
		Water samples				
Steam condensate						
Filtered	3,900	10,100	3,800	3,450	3,300	8,600
Unfiltered	5,200	12,000		3,990		
Cooling tower water						
Filtered	850	3,900	3,000	990	720	2,100
Unfiltered	1,300	6,100	8,550	990	1,400	12,800
Brine	49					
Evaporation pond	23					
		Gas samples				
Noncondensable gas (incoming steam)	300*	5,800†	> 4,000	2,500‡	1,800§	1,800
Ejector off-gas	190‖	< 10	> 400¶	65#	50	83
Cooling tower exhaust air	0.56**	0.59††	1.3‡‡	0.18	0.20	0.93‡‡
Ambient air	0.068	0.001§§	0.001§§	0.001§§	0.001§§	0.001§§

*60 percent Hg^0 and 40 percent Hg^{2+}. †72 percent Hg^0 and 23 percent Hg^{2+}. ‡79 percent Hg^0 and 21 percent Hg^{2+}. §78 percent Hg^0 and 22 percent Hg^{2+}. ‖92 percent Hg^0 and 8 percent Hg^{2+}. ¶> 84 percent Hg^0 and < 16 percent Hg^{2+}. #88 percent Hg^0 and 12 percent Hg^{2+}. **87 percent Hg^0 and 13 percent Hg^{2+}. ††84 percent Hg^0 and 16 percent Hg^{2+}. ‡‡These values are probably anomalously high because of mercury contamination of sampling equipment and the mercury analyzer used in earlier measurements in noncondensable gases containing high mercury levels. §§Mercury concentrations in ambient air away from the generating units at The Geysers ranged from < 0.001 to 0.018 ng/liter. However, the majority of the measurements indicated that mercury was present at concentrations very near the detection limit of 0.001 ng/liter.

500-Mwe complex at The Geysers geothermal field in California and the 75-Mwe power plant at Cerro Prieto, Baja California, Mexico.

The Geysers geothermal field is located approximately 110 km north of San Francisco in the Mayacmas Mountains of the California Coast Range. The Geysers geothermal power plants are of particular interest in this study since this geothermal area is located within one of the most productive mercury mining districts in the United States (*14*). More than 16 million kilograms of mercury have been extracted from over 20 mines in the eastern Mayacmas region. Geothermal exploration in extensions of The Geysers field disclosed dry steam from wells adjacent to numerous mercury mines (*5*).

The geothermal reservoir at The Geysers contains steam at initial temperatures and pressures of 250°C and 32 bars absolute. The steam is mobilized through fractures in Franciscan graywacke, a type of sandstone common to this area (*5, 15*). At The Geysers, 11 steam turbines supplied by 75 wells provide an electrical generating capacity of about 500 Mwe. Steam is supplied to the turbines at a temperature of about 180°C and a pressure of 7.9 bars absolute. About 4000 metric tons of steam per hour are required for operation of all the turbine generators of the 11 generating units. Steam is piped from the wells to the power plants, and after leaving the turbines the steam flows to direct-contact condensers. Noncondensable gases are removed by steam-jet gas ejectors, and currently the emissions from these gas ejectors are vented to the cooling towers to help accelerate the oxidation of H_2S. The condensed steam is pumped from the condenser to the cooling tower. In the power cycle, about 80 percent of the steam flow to the turbines is evaporated in the cooling towers and the excess condensate water is reinjected into the geothermal reservoir.

The Cerro Prieto geothermal field is located in northern Baja California approximately 35 km south of Mexicali. Fifteen wells supply steam to drive two turbines and generators, which supply 75 Mwe of electricity. The Cerro Prieto field is a hot water–dominated reservoir. The fluid in the producing strata (alternating layers of shale and sandstone) exists as the water phase and is under a pressure slightly higher than hydrostatic and a temperature averaging about 270°C. As the water flows toward the surface the pressure decreases and the steam phase is formed. At the wellheads the fluid is a mixture of about 70 percent by weight of very hot water and about 30 percent by weight of steam. The water has a dissolved solids content of approximately 2 percent. The steam is separated from the hot water at the wellheads in centrifugal separators and piped to the power plant, and the hot water is discharged to a large evaporation pond. The steam pathway through the power plant is essentially the same as that at The Geysers. The power plant utilizes 740 metric tons of steam per hour, resulting in 1600 tons of brine per hour.

To establish mass balances of mercury entering and leaving the power plants and to determine the chemical speciation of mercury, samples of incoming steam were condensed and the condensates and noncondensable gases were sampled. The power plant effluents consisting of cooling tower waters, cooling tower exhaust air, ejector off-gases, and brine waters were also collected for analyses. Mercury, a number of other difficult to preserve constituents, and several parameters were measured immediately after sampling in a mobile laboratory contained in a converted camper–pickup truck. These included H_2S, NH_3, F^-, dissolved S^{2-}, *p*H, oxidation-reduction potential (*Eh*), and various chemical forms of mercury. Mercury in solution was determined by a modified flameless atomic absorption procedure (*16*). Mercury concentrations in gases and chemical forms of volatile mercury were determined by collection of mercury on selective absorbents developed by Braman and Johnson (*17*), followed by volatilization and flameless atomic absorption analysis. The H_2S concentrations were determined in gases by using a Delmar Scientific H_2S analyzer and in ambient air by using a Meloy sulfur gas analyzer. Dissolved sulfide, fluoride, ammonia, *p*H, and *Eh* were measured by specific ion electrode techniques. Samples of liquids and gas scrubber solutions were collected and preserved for laboratory analyses of a variety of other major and trace constituents.

The mercury concentrations and chemical forms in the various geothermal fluids and power plant emissions are summarized in Table 1. The values shown in Table 1 are average concentrations of at least duplicate measurements of most samples. Mercury concentrations in steam condensates and cooling tower waters (which are made up from

Table 2. Mercury mass balance through several geothermal power plants.

Source	Mercury flux (g/hour)			
	Cerro Prieto (75 Mwe)	The Geysers		
		Unit 3 (27 Mwe)	Unit 8 (53 Mwe)	Unit 7 (53 Mwe)
Incoming mercury				
Condensable	3.8	1.7	1.4	1.8
Noncondensable	2.3	3.0	1.3	2.1
Total	6.1	4.7	2.7	3.9
Outgoing mercury				
Off-gas ejector	1.4	*	0.04	0.05
Cooling tower exhaust air	5.4	1.8	1.5	1.4
Reinjection	0	0.1	0.1	0.05
Discharge to surface waters	0.6	0	0	0
Total	7.4	1.9†	1.64‡	1.5§

*Vented to cooling tower. †Assumed 2.8 g/hour deposited with cooling tower sludge. ‡Assumed 1.3 g/hour deposited with cooling tower sludge. §Assumed 1.3 g/hour deposited with cooling tower sludge.

steam condensates) ranged from 720 to 12,800 ng/liter, roughly 100 to 1000 times higher than the concentrations in most uncontaminated river, lake, or ocean waters. At The Geysers power plants mercury present in the incoming steam was predominantly in the vapor state, and approximately one-half to two-thirds of the mercury remained as a noncondensable vapor when the steam was condensed. The mercury that condensed appeared to be present primarily in a dissolved form, or at least in a form not retained on 0.3-μm membrane filters. It did not appear to be present as elemental mercury, Hg^0, since it could not be purged from solution with nitrogen gas. In fact, the mercury appeared to be tightly complexed or possibly bound in a colloidal form, since only a small fraction could be readily reduced and volatilized by the addition of $SnCl_2$. Only after the addition of the powerful reducing agent sodium borohydride or after hot oxidation with HNO_3, $KMnO_4$, and $K_2S_2O_8$ could the mercury be freed to react with the $SnCl_2$. Since dissolved sulfide ion concentrations in the fresh condensate were found to be quite high—from 48 to 238 parts per million (ppm)—it may be possible that the mercury was complexed as a soluble sulfide species or existed as a colloidal or molecular mercury sulfide. The *p*H and *Eh* conditions measured in the steam condensates at The Geysers and Cerro Prieto suggests the presence of HgS_2^{2-} or $Hg(HS)_2^0$ aqueous species, according to the *p*H-*Eh* diagrams of similar systems by Hem (*18*). Also, the ammonia, which was present at relatively high levels (116 to 667 ppm) in the condensate, might form strong complexes with mercury.

At Cerro Prieto the mercury predominantly follows the steam phase as a vapor when the brine and steam are separated at the wellheads. Only about one-third of the mercury remains as a noncondensable vapor when the steam is condensed. Mercury levels in the steam condensate and cooling tower water at Cerro Prieto are comparable to those observed at units 7 and 8 at The Geysers.

At both locations, the cooling tower effluent waters contained about one-fourth as much mercury as the steam condensates that enter the cooling towers. This suggests that much of the mercury sent to the cooling towers in warm condensate is volatilized during the cooling processes. This is particularly evident at Cerro Prieto. Part of the mercury may also be scavenged from the cooling tower water by sulfur-containing particles present in the water which settle to the bottom in the cooling towers.

Mercury concentrations in the noncondensable gases from the incoming steam at The Geysers and Cerro Prieto ranged from 300 to 5800 ng per liter of gas. These concentrations are 10^5 to 10^6 times higher than mercury levels in the ambient air. Mercury concentrations in the ejector off-gases were considerably lower than in the noncondensable gases in the incoming steam. This is probably a reflection of the two different condensing systems used. The ejector off-gases consist of gases that do not condense in the power plant's direct-contact condensers, which function by spraying cooling tower water on the steam after it leaves the turbines. The noncondensable gases in the incoming steam were separated by condensing steam in small surface condensers used for routine sampling of gases and condensates at the power plants. The scrubbing afforded by the direct-contact condensers appears to scavenge some of the mercury present in a vapor form. Mercury levels in cooling tower exhaust air ranged from 0.18 to 1.3 ng/liter, compared to ambient air levels of approximately 0.001 ng per liter of air. The much lower mercury levels in the cooling tower exhaust air compared to the noncondensable gases are due to the extremely large dilution with ambient air.

The dominant form of volatile mercury in all gaseous samples was elemental Hg^0 vapor (see Table 1). The other forms of volatile mercury have not been absolutely identified and are listed as Hg^{2+} compounds. In this work, selective mercury vapor sorption traps, which were designed and tested to quantitatively separate and trap Hg^0 vapor, mercury chloride vapor, methyl mercury chloride vapor, and dimethylmercury vapor, were employed. However, additional volatile mercury compounds (perhaps sulfides) may be present in these geothermal gases and their uptake on our adsorbent traps is not yet known. Laboratory tests are being conducted to evaluate the actual chemical species present and the possible effects of various interferences.

It was surprising to observe mercury occurring in the incoming noncondensable gases and in the ejector off-gases as Hg^0 vapor when H_2S levels in these gases were so high, ranging from 1.0 to 5.7 percent. Apparently, the elevated temperatures and reducing environment, together with the high vapor pressure of Hg^0, permit the mercury to exist unassociated with the high sulfide levels.

Table 2 presents mass balances of mercury entering and leaving the Cerro Prieto power plant and The Geysers generating units 3, 7, and 8. The balance is based on measured mercury concentrations in incoming and outgoing effluents together with mass flow rate data supplied by the operators. Mass balances for mercury at The Geysers units 4 and 11 are not listed; the mercury concentrations measured in their cooling tower exhaust air during our first field trip were probably anomalously high because of cross-contamination of the mercury analyzer and equipment during earlier measurements of high mercury levels in noncondensable gases.

At Cerro Prieto an excellent mass balance for mercury was obtained. A total of 6.1 g of mercury per hour was measured entering the plant, and 6.8 g/hour was accounted for in the effluents leaving the plant. Most of the mercury leaves in the cooling tower exhaust, where 5.4 g/hour escapes to the atmosphere. The off-gas ejectors release 1.4 g/hour to the atmosphere. About 0.6 g/hour is discharged to the evaporation pond with the separated brine.

At The Geysers units 3, 7, and 8 more mercury was measured entering the units than could be accounted for in the various effluents. Unit 3 has the greatest mercury influx, and on a per megawatt basis receives 3½ to 2½ times more mercury than units 7 and 8, respectively. Only 40 to 60 percent of the incoming mercury was accounted for in releases to the atmosphere, with the cooling tower exhaust air being the dominant pathway. Reinjection of excess condensate (cooling tower water) into the geothermal reservoir removed only 0.05 to 0.1 g of mercury per hour. The mercury imbalance at The Geysers could very well be accounted for in the sludge that deposits in the bottom of the cooling towers and must be periodically disposed of in certified landfills. This sludge, which is composed primarily of sulfur from the oxidation of H_2S, contains 0.02 to 0.2 percent mercury. It is difficult to obtain quantitative estimates of the rate of formation of the sludge, but this appears to be an important scavenging mechanism for mercury at The Geysers.

It is of interest to compare the mercury emissions from geothermal power plants with those from coal-fired power plants. Billings *et al.* (*19*) report that a 700-Mwe coal-fired unit releases about 2.3 kg of mercury to the atmosphere each day. On a per megawatt basis this amounts to 3.3 g Mwe^{-1} day^{-1}. At two other coal-fired power plants much lower atmospheric mercury emissions of approximately 0.50 and 0.48 g Mwe^{-1} day^{-1}, respectively, were reported (*20, 21*). Atmospheric mercury emissions from the Cerro Prieto geothermal power plant and from The Geysers units 3, 7, and 8 amounted to 2.2, 1.6, 0.70, and 0.66 g Mwe^{-1} day^{-1}, respectively. Thus, on a per megawatt (electric) basis, the atmospheric releases of mercury from geothermal power plants are roughly comparable to those from coal-fired power plants.

At present there are no Environmental Protection Agency (EPA) mercury emission standards for energy generating facilities. However, the EPA has set a national emission standard for mercury smelters and chlor-alkali plants, which is that the mercury emissions are not to exceed 2300 g released to the atmosphere per 24-hour period (*22*). The atmospheric mercury emissions from 25- to 75-Mwe geothermal power plants (36 to 144 g/day) are far below this standard.

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Stable Semiconductor Liquid Junction Cell with 9 Percent Solar-to-Electrical Conversion Efficiency

Abstract. *The semiconductor liquid junction cell* n-*GaAs/0.8*M *K_2Se-0.1*M *K_2Se_2-1*M *KOH/C has been shown to attain 9 percent photovoltaic power conversion efficiency in sunlight. Accelerated tests under 3100°K light sources of several solar intensities indicate very low photocorrosion currents and high output stability.*

We describe the stable operation of a semiconductor liquid junction solar cell which converts solar to electrical power at 9 percent efficiency. The cell consists of an *n*-type GaAs electrode, a carbon counterelectrode, and an aqueous solution of the Se^{2-}/Se_2^{2-} redox couple. The electron-hole pair generated on illumination of the semiconductor is separated by the field near the solution interface (*1*), with the hole moving toward the solution and the electron moving through the bulk of the semiconductor and then through an external load to the counterelectrode. As a result, the illuminated electrode becomes an anode and the counterelectrode a cathode. In a well-behaved cell the oxidation and reduction processes at the two electrodes balance, producing no net chemical change in the solution.

Central to the realization of the concept of these cells is the demonstration of efficient conversion of light to electrical power and of stable operation.

Semiconductor liquid junction solar cells that are based on the *n*-type cadmium chalcogenides CdS (*1–4*), CdSe (*3, 5, 6*), and CdTe (*7*) in the redox electrolytes S^{2-}/S_2^{2-}, Se^{2-}/Se_2^{2-}, and Te^{2-}/Te_2^{2-} have been reported. With several of these combinations, oxidative photoetching of the semiconductor surface under illumination is substantially eliminated (*3, 4, 6, 7*). We have found that the cell CdSe/1*M* Na_2S-1*M* S-1*M* NaOH/C shows an efficiency of 7 to 8 percent for energy conversion at an insolation of ~ 75 mw cm^{-2} (*8*), but this level drops on extended irradiation under load in spite of the apparently minimal evidence of photoetching. We find that the solar cell *n*-CdTe/0.8*M* K_2Se-0.1*M* K_2Se_2-1*M* KOH/C also attains an efficiency near 8 percent. In this case the semiconductor photoetches concurrently at a low rate, but at one sufficient to seriously limit practical life.

We now report that the single-crystal *n*-GaAs/0.8*M* K_2Se-0.1*M* K_2Se_2-1*M* KOH/C solar cell has the highest efficiency so far observed by us (9.0 ± 0.5 percent at an insolation near 70 mw cm^{-2}), yet is sufficiently stable with respect to both photoetching and power output to suggest an effective life of several years. The band gap of GaAs (1.42 ev) is very near the optimum for photo-