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Hao-Lin Chen

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Laser Cleanup of Pt Group Metals*

Hao-Lin Chen

University of California
Lawrence Livermore Laboratory
P.O. Box 808, Livermore, California 94550

Due to increasing interest in chemical and fuel synthesis from syngas, we have recently re-evaluated the feasibility and practicality of purifying Pt group metals (Pd, Ru, Rh) using LIS technologies. Our findings for the ^{107}Pd cleanup are described here.

OBJECTIVES

As discussed in the 1978 annual, Pd, Rh and Ru metals are produced in significant quantities as fission products in nuclear reactors. These metals are commonly used as catalysts for reforming petroleum products and for producing nitric oxide and glass fibers. Currently, we import about 95% of the Pt group metals from the USSR and South Africa. Thus it is strategically important for us to be able to produce these materials domestically. Unfortunately, the reactor-produced Pt group metals contain small amounts of harmful radioactive isotopes. These must be removed before the metal can be used as a catalyst in industry. It is here where we see the AIS technology might be able to make some impact to the "Synfuel" program in the foreseeable future.

At this time, there is no economic incentive for extracting the Pt group metals from nuclear wastes. Taking Pd metal as example, the

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mid-1979 market value is about \$3.50/g while the estimated "non isotopic" recovery costs (from nuclear reactor wastes) will run about \$12.30/g (Exxon Nuclear Company Report, 1978 DOE, EY-77-C-06-1013) which is four times of the current value of the imported Pd.

It appears from this study that removal of these harmful radioactive isotopes from the reactor-produced Pt group metals could be achieved using a LIS technique. The proposed technique for ^{107}Pd removal (the harmful isotope in the Pd metal) is briefly described here.

PREVIOUS FINDINGS

A preliminary LIS feasibility study for the Pt group metals has been made earlier by Worden, et. al (IS-76-216, 436). As they pointed out, simple atomic-vapor photoionization process as developed for the uranium isotope separation program did not appear to be directly applicable to the Pt group metals. Since the isotope shift of these metals is much narrower than the doppler broadened visible absorption widths, it is difficult (if not impossible) to achieve any kind of selectivity without resorting to a Doppler-free technique.

THE PROPOSED SCHEME FOR Pt GROUP METALS

The technique described here is very similar to that proposed by Balling and Wright (Appl. Phys. Lett. 29, 411, 1976) for separating isotopes having different nuclear spins and hyperfine structures. The selectivity of this technique relies on the angular momentum selection rules for atomic absorption of circularly polarized light. In principle,

The selection rules for atomic absorption of left-circularly polarized laser light are

$$\Delta M_J = +1 \quad \text{for the even isotopes, } I = 0 \quad ({}^{104}\text{Pd}, {}^{106}\text{Pd}, {}^{108}\text{Pd}, {}^{110}\text{Pd})$$

$$\Delta M_F = +1 \quad \text{for the odd isotopes, } I = 5/2 \quad ({}^{107}\text{Pd}, {}^{105}\text{Pd})$$

where $F = I + J$. Note the photoionization selectivity relies on the absorption cross section for the second transition (${}^3P_1 \rightarrow {}^3P_0$ at 5210 Å), which is zero for the even isotopes.

The apparent limitation on the selectivity of this purification process appear to be:

a. The degree of circular polarization that can be achieved in the two laser beams (λ_1 and λ_2). The presence of an incorrect polarization such as right-circularly polarization will result in an unwanted excitation of even isotopes with $I = 0$.

b. The collinearity of the two laser beams (λ_1 and λ_2). If the two beams are not perfectly collinear, an even isotope with $I = 0$ excited to the $M_J = 1$ level of the 3P_1 state would have a non-zero probability of being in the $M_J = -1$ level relative to the axis of the quantization defined by the second beam, enabling it to make a $\Delta M_J = +1$ transition.

c. The oscillator strength of the second transition (${}^3P_1 \rightarrow {}^3P_0$ at 5210 Å), which determines the minimum laser intensity required for effective removal of the odd isotopes out of the 3P_1 level. If the required laser power is too high, some fraction of the even isotopes might also be excited through multi-photon processes under the influence of the intense laser field.

TECHNICAL ISSUES

There are two scientific issues pertaining to the economics of this purification process. One is the optical selectivity of the first transition, $^1S_0 \rightarrow ^3P_1$ at 2763 Å, or the degree of unwanted laser adsorption by the even isotopes ($I = 0$) and ^{105}Pd . The other one of equal importance is the oscillator strength of the second transition $^3P_1 \rightarrow ^3P_0$ at 5210 Å for the odd isotopes (^{107}Pd and ^{105}Pd) with $I = 5/2$. It is important that a large fraction of the ^{107}Pd isotopes can be effectively removed in relatively small a number of stages.

Figure 2 is a composite atomic absorption spectra (λ_1 , $^1S_0 \rightarrow ^3P_1$ at 2763 Å) for the Pd metal recovered from the reactor waste. The initial isotopic composition is 18% ^{107}Pd , 19% ^{104}Pd , 23% ^{105}Pd , 26% ^{106}Pd , 12% ^{108}Pd and 3% ^{110}Pd .

The isotope shift for the 2763 Å transition is roughly 8 mK (10^{-3} cm $^{-1}$) per mass change. The nuclear spins of ^{107}Pd and ^{105}Pd are identical; $I = 5/2$. We assume that the nuclear structure and the nuclear quadrupole moments for ^{107}Pd and ^{105}Pd are also similar (within $\pm 20\%$) which allows us to make estimates for the hyperfine coupling constants (A and B) and hyperfine splittings for ^{107}Pd .

It might be possible to attain some selectivity on the first step using a single mode pulsed dye laser tuned to a region between the hyperfine absorption features of ^{107}Pd ($F = 5/2 \rightarrow 5/2, 5/2 \rightarrow 7/2$). Since ^{105}Pd also has a nuclear spin of $5/2$, some fraction of the ^{105}Pd will also be excited and ionized along with the ^{107}Pd . We estimated that roughly 83% of the excited ^{107}Pd (3P_1) can be further excited to the 3P_0 level and hence ionized by λ_3 . In principle 65% of the ground ^{107}Pd atoms can be ionized per stage. For achieving a final ^{107}Pd concentration of 2.2% (an acceptable level for industry), a minimum of two stages are necessary.

The oscillator strengths of the second (λ_2) and third (λ_3) transitions are not known. Clearly, the first priority of future work on ^{107}Pd cleanup is to map out transitions which have acceptable strengths for the second and third steps when using circularly polarized laser light. Assuming that adequate transitions are found, we can then make a more realistic cost analysis for the purification process.

We have made a crude estimate for the cost of ^{107}Pd cleanup using the LIS technique described here. The cost-increase for Pd recovery (from nuclear wastes) due to the addition of laser purification process is roughly 1-2 \$/g which amounts to roughly 10% of the final product value, 12.3 \$/g (estimated by Exxon Nuclear Inc., 1978).