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Zinc Mitigation Interim Report – Thermodynamic Study

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Summary

A review of phase diagrams, literature, and thermodynamic calculations was conducted to determine if there are suitable materials to capture zinc vapor within the lithium trap of the extraction basket. While numerous elements exist that form compounds with zinc, many of these also form compounds with hydrogen or the water that is present in the TPBARs. This relatively comprehensive review of available data indicates that elemental cobalt and copper and molybdenum trioxide (MoO_3) may have the requisite properties to capture zinc and yet not be adversely affected by the extraction gases and should be considered for testing.

Background

An experimental program was initiated in order to develop and validate conditions that will effectively trap Zn vapors that are released during extraction. The proposed work is broken down into three tasks. The first task is to determine the effectiveness of various pore sizes of filter elements. The second task is to determine the effect of filter temperature on zinc vapor deposition. The final task is to determine whether the zinc vapors can be chemically bound. The approach for chemically binding the zinc vapors has two subtasks, the first is a review of literature and thermodynamic calculations and the second is an experimental approach using the best candidates. This report details the results of the thermodynamic calculations to determine feasibility of chemically binding the zinc vapors within the furnace module, specifically the lithium trap (1).

Method

The primary methods used were the computer program HSC Chemistry 7.0 (2) and a review of Binary Phase Diagrams (3) to determine which elements may react with metallic zinc vapors to form stable compounds at the temperature and pressures of interest. The first step was to determine which elements formed compounds with zinc and both the program and phase diagrams were consulted. This list was then vetted against hydride forming elements. The presence of hydrogen isotopes in the TEF will present challenges for strong hydride formers since there are large quantities of hydrogen and minor quantities of Zn competing for the same materials. If the reactions appeared to be favorable, thermodynamic calculations were performed to see if there were possible temperature and pressure conditions that would enable capture of the zinc vapors and not have other adverse impacts. Both equilibrium compositions were calculated as well as Temperature Partial Pressure (TPP) calculations. Both of these calculations are relatively easy with the HSC Chemistry program.

Results

Base on the phase diagram and computer program assessments, a significant number of elements were found that will react with zinc to form stable intermetallic compounds. The potential zinc compound forming elements are listed in Table 1. This list gets progressively smaller as one eliminates radioactive, reactive, and toxic elements based on safety and waste disposal issues. The list is further decreased due to the elimination of the high vapor pressure materials that may be volatilized and thus present additional challenges for the TEF. The hydride forming elements and remaining elements deserve further consideration and are addressed subsequently.

Table 1. Potential candidate elements that form zinc compounds.

Zinc Compound Forming	Radioactive, Reactive and Toxic	High Vapor Pressure	Hydride Forming	Remaining
Ag, As, Au, Ba, Ca, Ce, Co, Cr, Cu, Dy, Er, Eu, Fe, Gd, Ho, K, La, Li, Lu, Mn, Mo, Na, Nb, Nd, Ni, P, Pd, Po, Pr, Pt, Pu, Rb, Ru, S, Sb, Sc, Se, Sm, Sr, Ta, Tb, Tc, Te, Th, Ti, Tl, Tm, U, V, Y, Yb, Zr	**As, Ce, Po, Pu, Te, Th, U, K, Na,**	**As, Ba, K, Li, Mg, Na, P, S, Sb, Sr, Se**	**Ag, Au, Ba, Ca, Ce, Cr, Cu, Dy, Er, Gd, Ho, K, La, Lu, Li, Mg, Na, Nb, Nd, Ni, P, Pd, Pr, Pu, Rb, Sm, Sc, Sr, Ta, Tb, Th, Ti, U, V, Y, Zr**	**Co, Mn, Mo, Pt, Ru**

Hydride Stability

Of the elements that form hydrides, one can refine the list into strong hydride formers, Ca (4) Dy, Er, & Gd (5), Ho & Lu (6) La (7) Ca, Na, Mg, Ti & Zr (8) Sc (9) La, Ce, Pr, Nd, Sm, Gd, and Er (10) hydrides that decompose above 200°C and less strong hydride forming elements. This list reduction results in the following elements that may be suitable for reacting with Zn vapors: Cu, (11) V, Nb, (12) and Pd (13). Copper cannot be fully vetted since the data do not exist in the HSC Chemistry program, however, based on the phase diagrams it may prove useful. There are other classes of multi-component materials that form less stable hydrides that are more complex than single elements. These include LANA (La-Ni-Al) (14) and other AB_5 compounds where A is La, Pr, Nd, Sm, Gd, or Y and B is Ni or Co (15) thus indicating that more complex chemistry may be useful to trap zinc without entraining hydrogen, however, the surface reactivity of the compounds must also be considered due to the presence of water during extraction.

Several metallic elements were considered as candidates for thermodynamic calculations; unfortunately, limited availability of Zn and H data in HSC Chemistry (2) significantly reduced the number of systems that could be calculated. The following elements, Y, Ca, Mg, U, Pr, Sm, were considered as candidates and equilibrium compositions were calculated for Zn, H, and the element. Subsequent to the equilibrium calculations, Temperature Partial Pressure (TPP) stability diagrams were created using the element, Zn, and hydrogen to determine if the low vapor of Zn would favor the hydride or the zinc compound formation. The characteristic results for Ca and Y are shown in Figures 1-4. The equilibrium diagrams, Figures 1 and 3, indicate that the hydrides of Ca and Y as well as YZn and CaZn are stable, results consistent with the literature review. However, the equilibrium diagrams are based on higher pressures of Zn than are actually suspected during extraction. Consequently, the TPP diagrams were generated for fixed H_2 pressures of 10^{-20}, 10^{-10}, 10^{-5}, and 10^{0} atmospheres. These results are shown in Figures 2 and 4 for Ca and Y, respectively. From these stability diagrams it is apparent that at very low pressures of Zn, which are expected in the TEF, the hydride phases will be stable while at very high pressures of Zn, the zinc compounds are stable. A further complication arises since both Y and Ca are very reactive with oxygen and water and consideration of the extraction gases indicates that approximately 30% of the hydrogen isotopes expected to be water, table 2. This condition will make it difficult if not impossible to maintain these materials elementally. Consequently, alternative materials or solutions need to be considered.

Non-metallic materials

One alternative strategy to entrap the Zn vapors is to utilize a non-metallic matrix such as an oxide. An ideal material of this nature would react with neither the hydrogen species nor the other gaseous species in the extraction gas. The presence of water, table 2, can pose problems since it may react with many of the metallic species and oxidize them especially since many of the potential candidate elements are fairly reactive.

Consequently, a review of zinc containing oxide spinels was conducted. During this review, it was found that Fe, Co, Cr, Mo, and W all formed favorable compounds and iron oxide, in particular Fe_2O_3 (hematite), forms a naturally occurring zinc spinel of the form $ZnFe_2O_4$ (17). This result was the basis of additional thermodynamic calculations using Ref 2. The equilibrium diagram for hematite – zinc with hydrogen at temperatures between 0 and 500°C is shown in Figure 5. It is apparent that all of the Zn can be transformed thermodynamically to an oxide compound in this temperature range. TPP diagrams for Zn and O_2 pressures at temperatures from 200 to 500°C were generated and are shown in Figure 6. As is the case for elemental capture of Zn, these results suggest that high Zn pressures may be needed to capture the zinc.

In order for the hematite to capture the Zn vapors, the iron must remain in the oxidized state. Consequently, a calculation was made to see if it could survive an extraction run. Unfortunately, it was calculated that Fe could be reduced by the hydrogen as it is extracted. The effect of mixing 130 moles of hydrogen with one Kg of Fe_2O_3 is shown in Figure 7. This diagram indicates that metallic iron could be formed at temperatures greater than about 250°C as a consequence of iron oxide reduction coupled with water formation.

As was indicated above, cobalt oxide also forms a spinel so a series of calculations were also made for this material. These results indicate that the CoO will be reduced during exposure. However, it was determined that the intermetallic compound CoZn could form.

Table 2. Gas species present in 300 TPBARs (16)

Species	Amount
Ar-37	.098 Ci 1 year after extraction
Ar-39	2.9 Ci after 90 days
T_2	60 moles
H_2	70 moles
He-4/He-3	18 moles
Q_2O (water)	40 moles of 130 hydrogen isotopes
CO	<0.1 moles
CO_2	<0.2 moles
CH_4	<0.1 moles
CH_3T	<0.1 moles

Non-Hydriding Compound Formers

Based on the reduction of the CoO to metallic Co and the CoZn compound, further assessment of the Co-Zn-O-H system was conducted. A typical equilibrium calculation for the Co-Zn-O-H system is shown in Figure 8 and the TPP diagrams for two hydrogen pressures are shown in Figure 9. Note that there is an invariant product condition for this system as a function of H_2 pressure since Co does not form a hydride, will not be oxidized by water vapor, and will form a CoZn intermetallic compound. Thus, it appears that elemental Co may be suitable for trapping Zn vapors.

The other potential, non-hydride forming elements, do not have data available in the software package and their stability cannot be as easily determined. The stability can be estimated using the relative stability of water and the oxides. If the oxides are more stable relative to water than it is likely that the metallic elements will be oxidized rather than being available for reaction with the Zn. Based on this simplified assessment, both Mo and Mn will be oxidized in the presence of the water/water vapor and will not be in a metallic state and be able to capture the Zn, but Mo oxide also forms a spinel with Zn. A series of TPP diagrams, shown in Figure 9, clearly show that MoO_3 and ZnO will react to form the spinel. Since the Zn vapors are released in the metallic (18) despite the presence of water, it is likely that they cannot be captured as spinels, unless a source of oxygen is added.

Ru and Pt are also stable relative to water but are relatively expensive precious metals and there cost precludes further consideration at this stage.

Discussion and Conclusions

Many metallic elements are apparently conducive to the formation of zinc intermetallic compounds. Unfortunately the majority of these elements are also hydride formers. Due to this feature, elements that are both hydride and zinc compound forming will tend to form the hydrides due to the prevalence of hydrogen and the relative dearth of zinc.

The presence of 40 moles of water in the 300 basket load of TBPARs further complicates the matter and materials that are more prone to oxidation than water will tend to be oxidized and again not be available for zinc capture. In addition, the limitation of the computer program with the appropriate data to predict relative stabilities forces suppositions that several other elements will be oxidized rather than remain metallic for the Zn reaction.

Of all the materials considered, it appears that elemental cobalt and copper and molybdenum trioxide may be able to capture elemental zinc and zinc oxide, respectively, and are inert and are inert relative to both water and hydrogen. These materials are readily available in numerous forms. Consequently, phase four of the Zinc Mitigation Development Strategy will include using elemental cobalt and copper and molybdenum trioxide based materials to determine if zinc compounds can be formed under suitable simulated conditions. The expectation that it will be possible to capture zinc and oxidize it on the molybdenum oxide, however, will require that the zinc oxidize during extraction. The forensic work for the zinc 65 deposit from cycle 6 indicated that metallic zinc was able to migrate well beyond the extraction basket (18), so this approach will be pursued, although its success seems unlikely without further additions to the zinc trap, such as an oxygen source.

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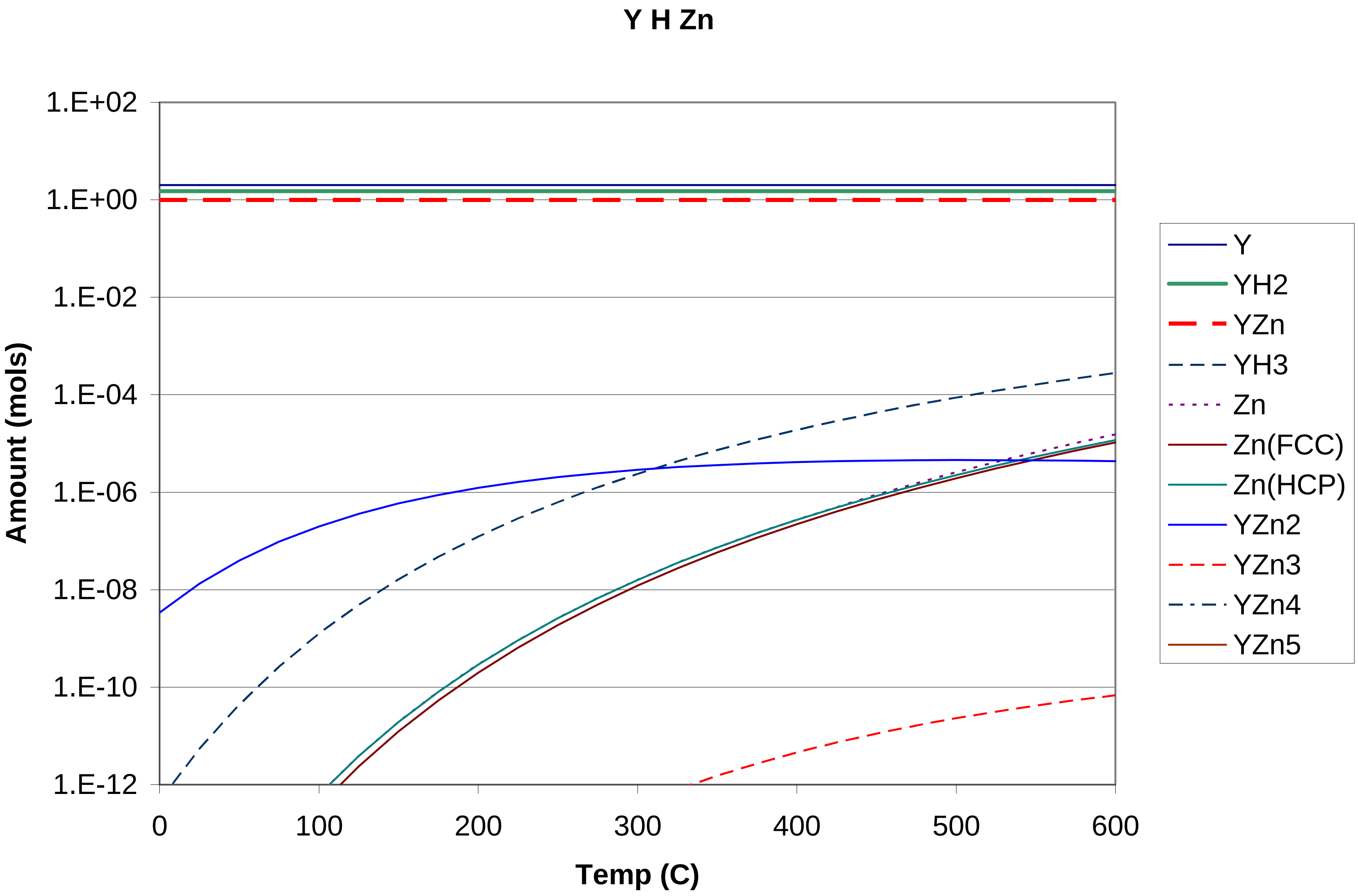

Figure 1. Yttrium – zinc – hydrogen equilibrium diagram. Note Y, YH_2, and YZn are the dominant species for 1.5 Mol H_2 4.5 Y, 1.0 Zn as input.

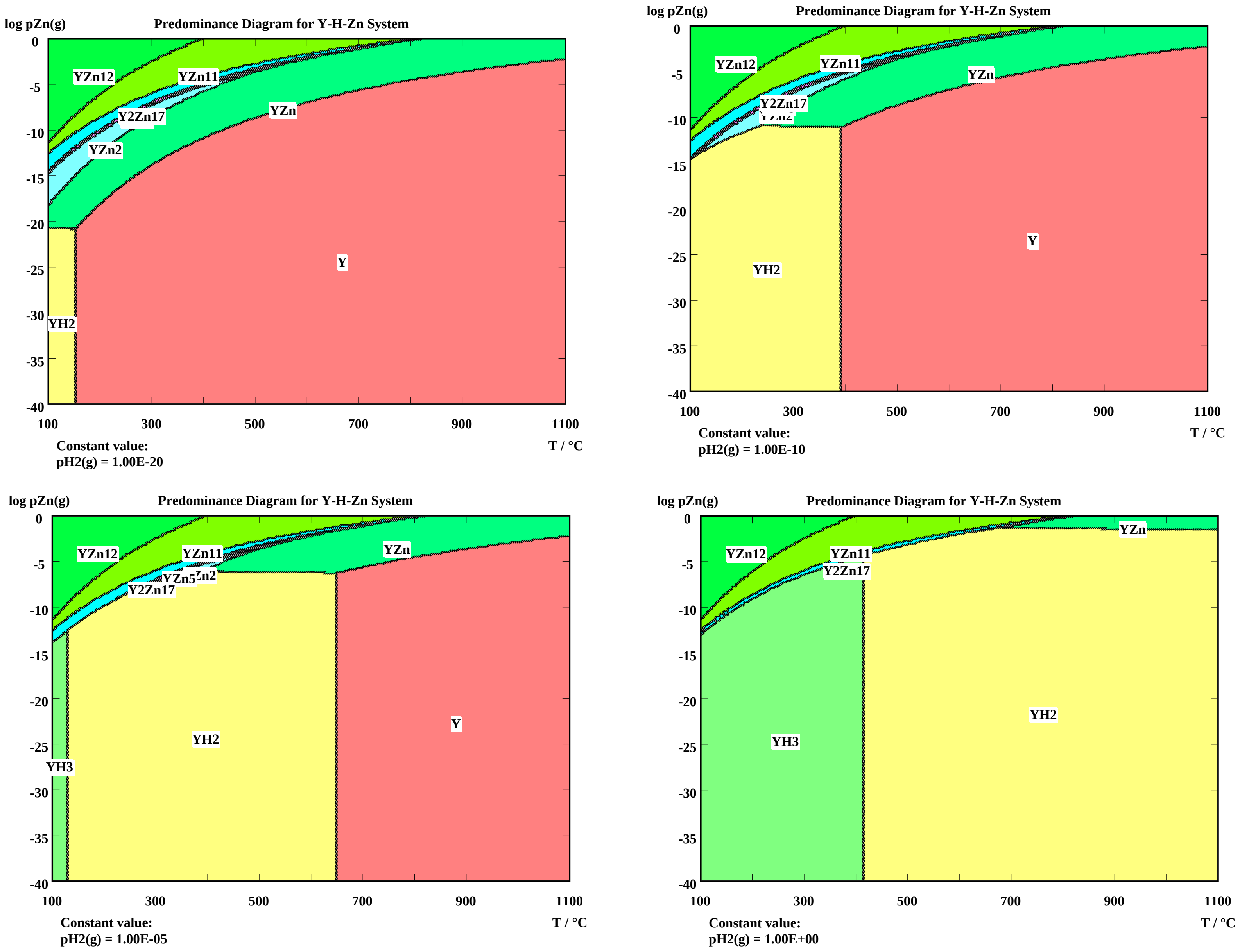

Figure 2. TPP of Y-H-Zn for low to high H_2 pressures.

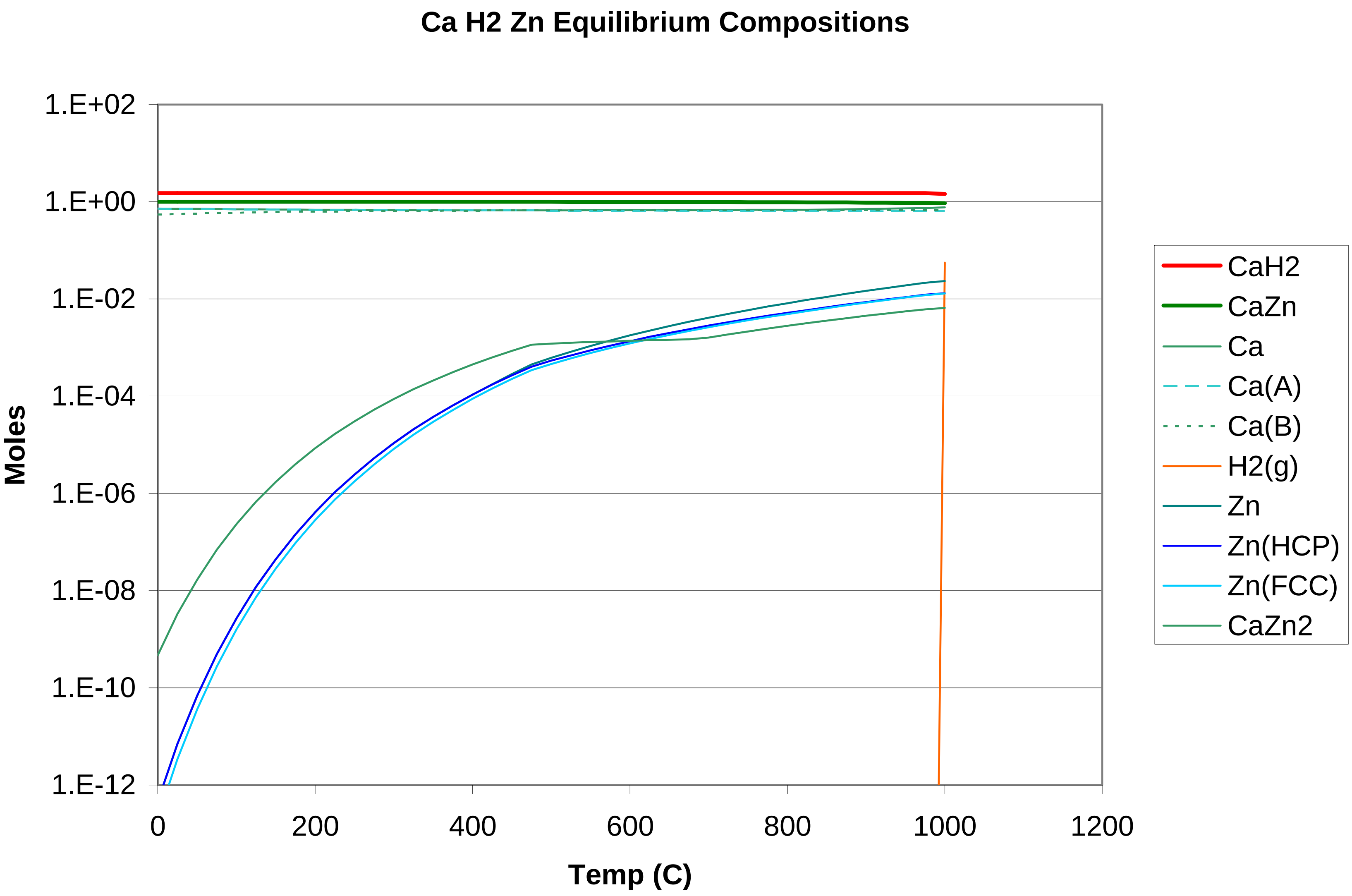

Figure 3. Calcium – zinc – hydrogen equilibrium diagram. Note Ca, CaH_2, and CaZn are the dominant species for 1.5 Mol H_2 4.5 Ca, 1.0 Zn as input.

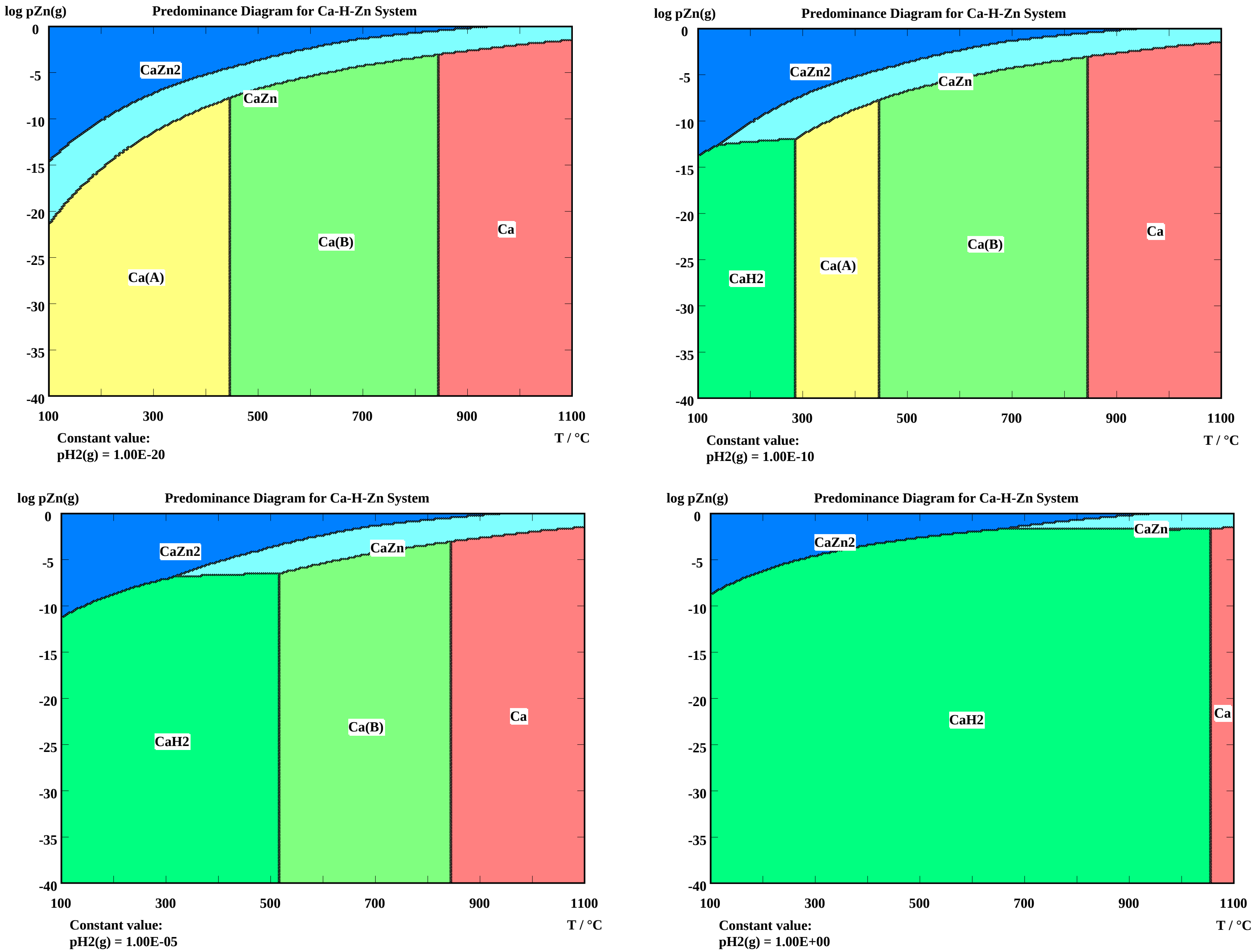

Figure 4. TPP of Ca-H-Zn for low to high H_2 pressures.

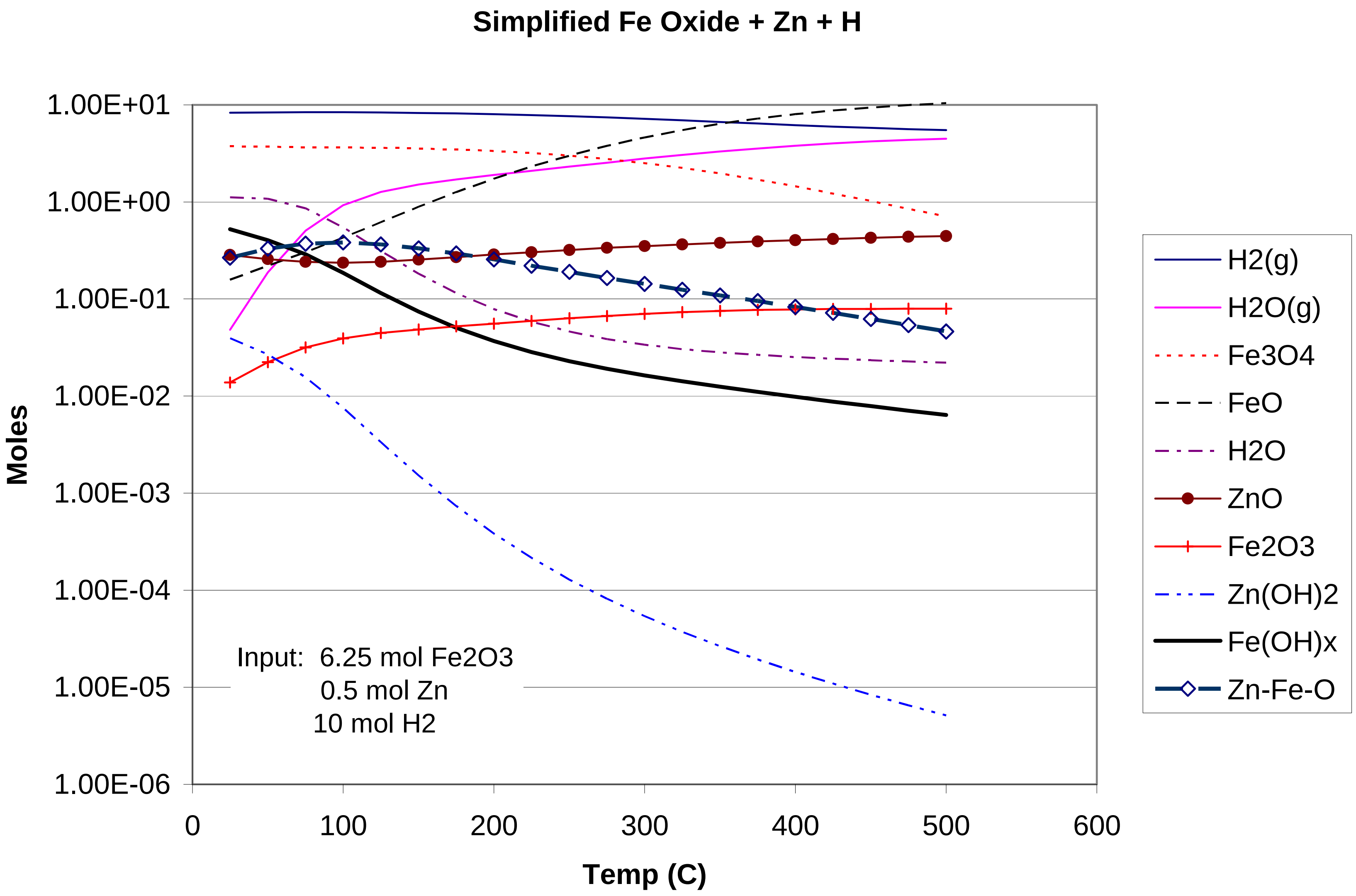

Figure 5. Simplified equilibrium diagram for Zn + Fe_2O_3 + H_2. Complex compounds were pooled to give Zn-Fe-O results rather than individual species.

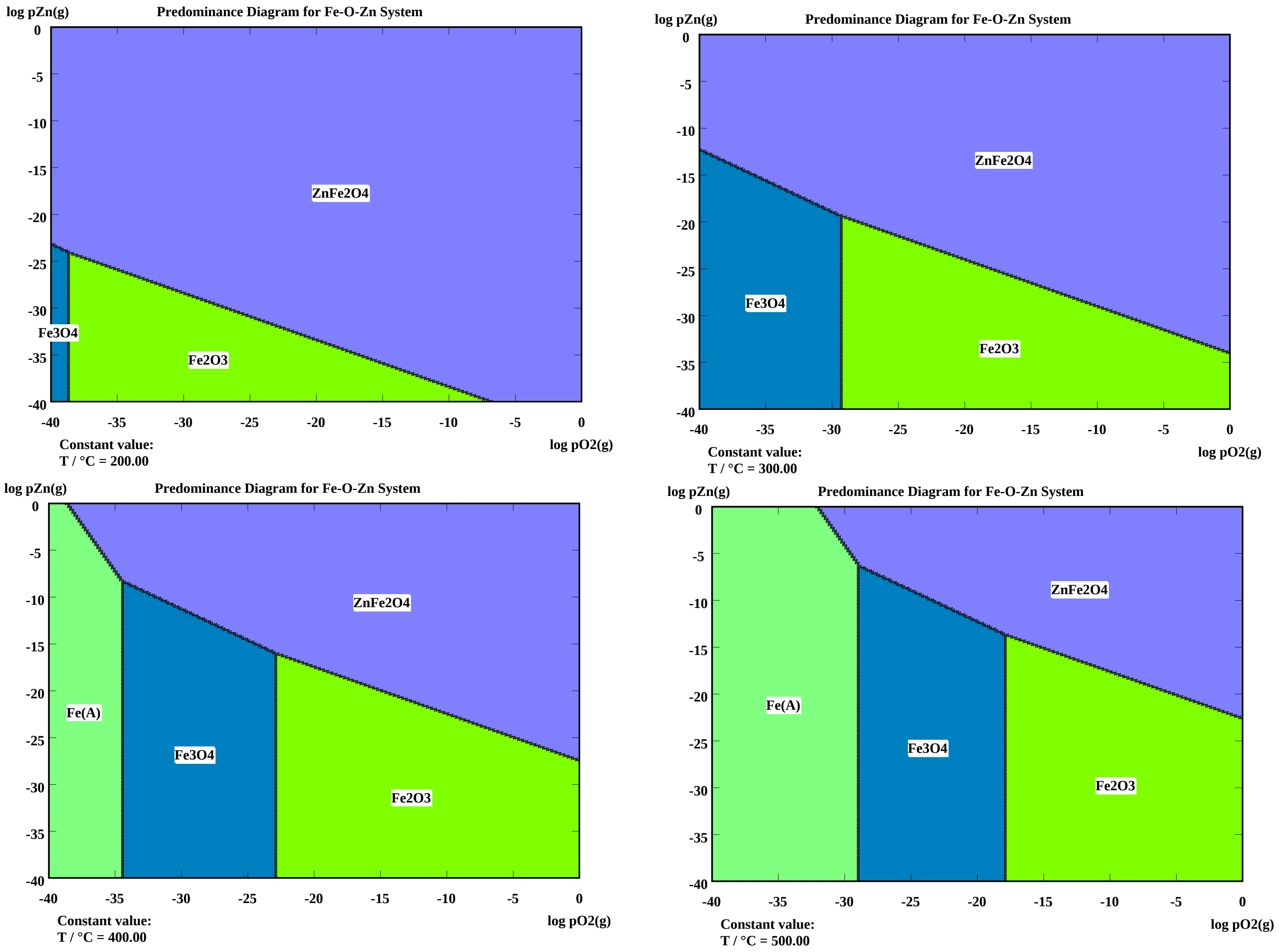

Figure 6. TPP for Zn Fe O at four temperatures.

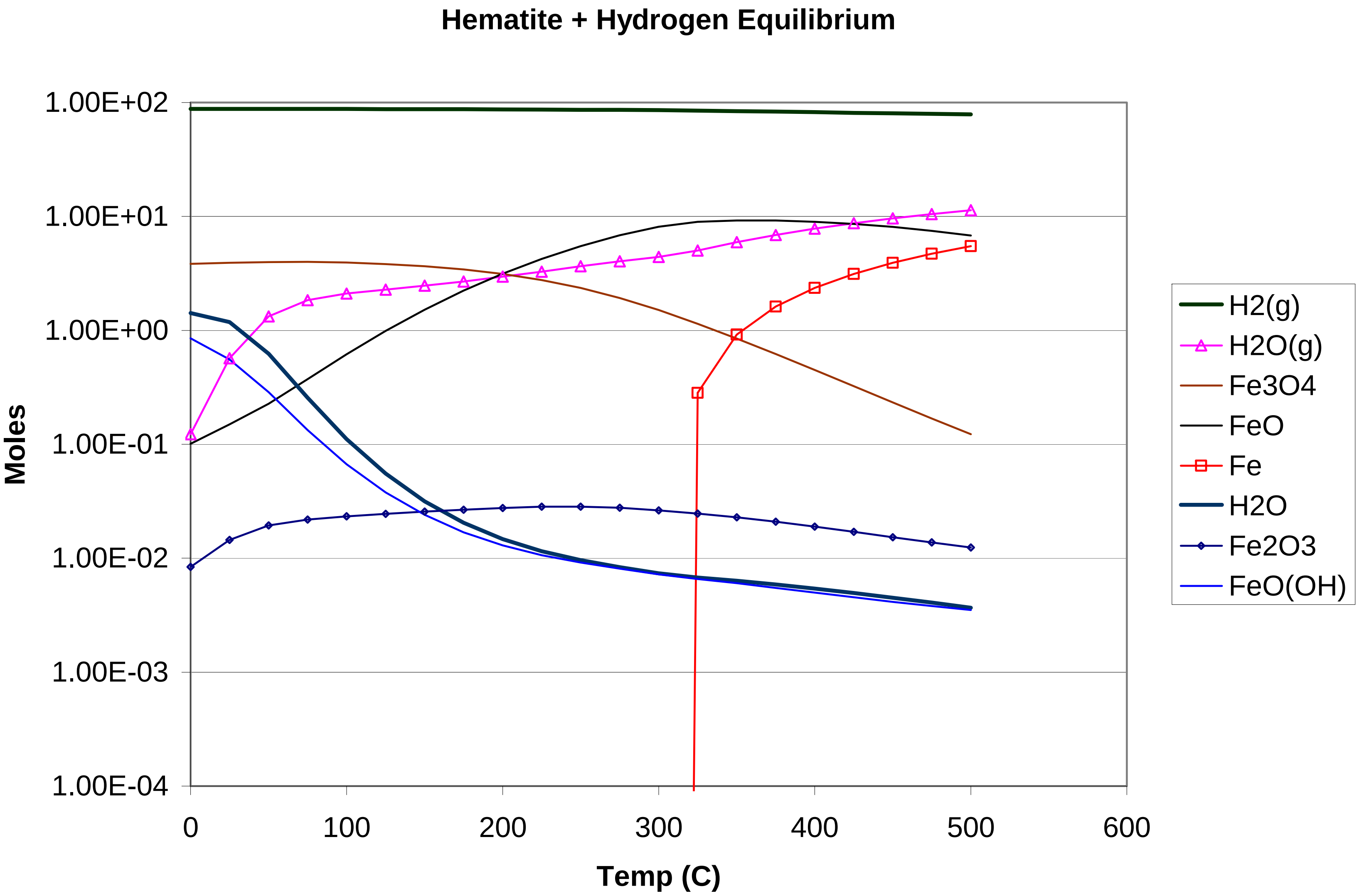

Figure 7. Equilibrium diagram for 6.25 moles of hematite and 90 moles of hydrogen.

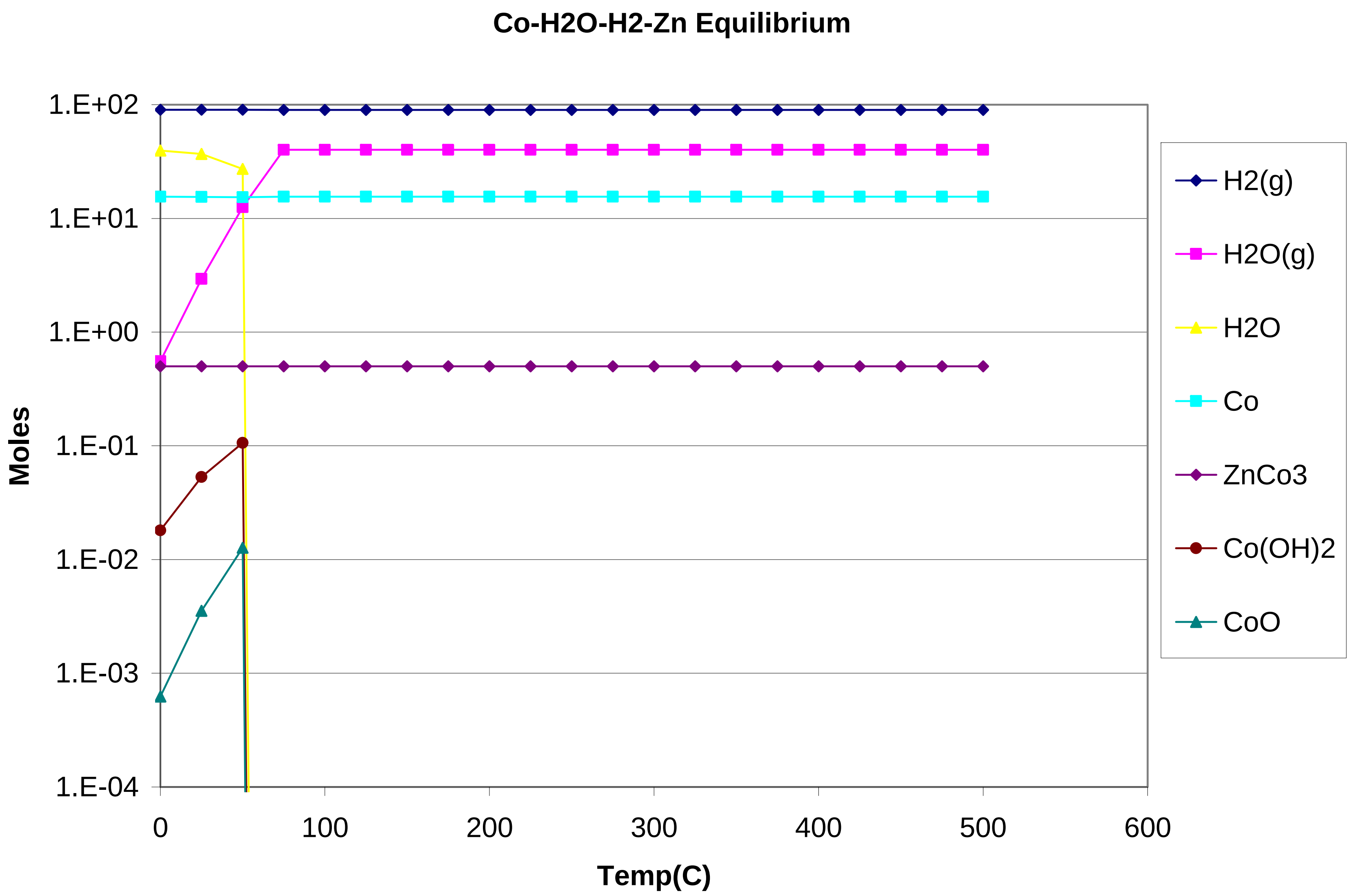

Figure 8. Equilibrrium Diagram for Co in the presence of water hydrogen and zinc.

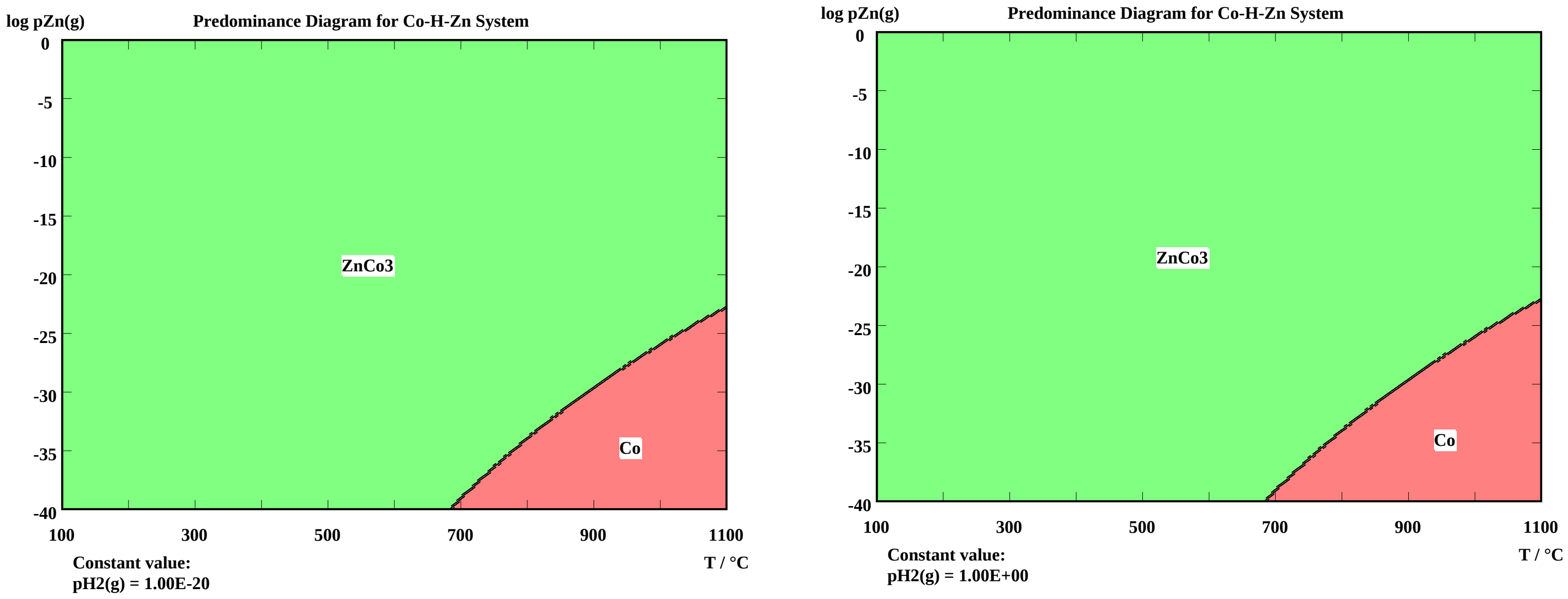

Figure 9. TPP diagrams for the Co-H-Zn system, a non-hydride forming material.

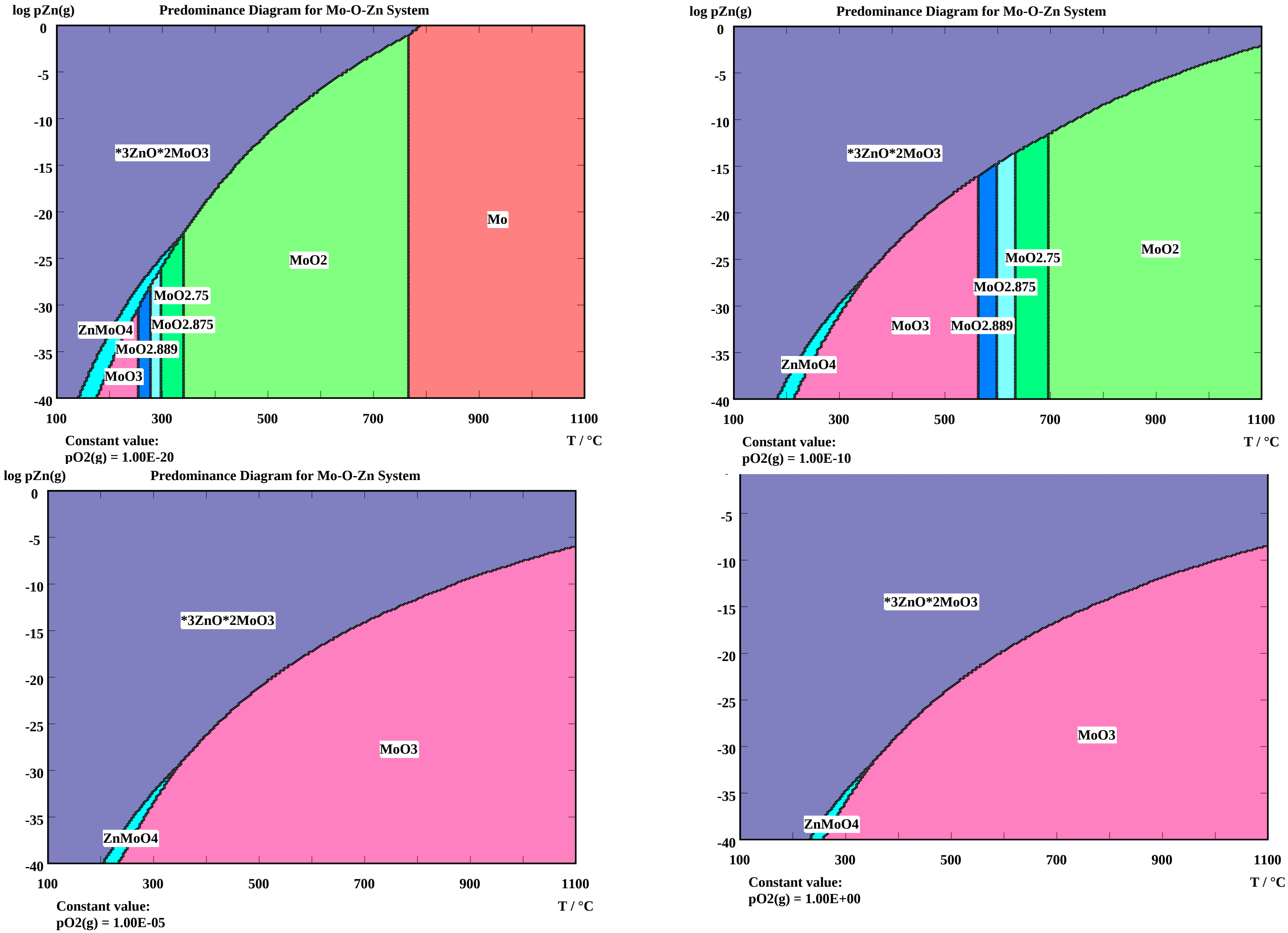

Figure 10. TPP diagrams for the Mo-O-Zn system