PERFORMANCE ANALYSIS OF COPPER CANISTER CORROSION UNDER OXIDIZING OR REDUCING CONDITIONS

KAREN WORGAN*, MICHAEL APTED* AND ROLF SJÖBLOM**
* Intera Information Technologies, Inc., Denver, Colorado 80235
** Swedish Nuclear Power Inspectorate, Stockholm, Sweden

ABSTRACT

The finite-difference CAMEO code for modeling general corrosion of copper canisters is described. CAMEO represents the engineered barrier system and surrounding fractured host rock in 3-dimensional cylindrical coordinates. The time of containment failure is evaluated using CAMEO, as constrained by transport rates of corrodants to the canister or by transport rates of corrodant products away from the canister. Additional chemical processes explicitly modeled in CAMEO include 1) copper corrosion, and 2) kinetics of Cu(I) oxidation to Cu(II), both as a function of near-field pore water chemistry, specifically pH, Eh, and chloride concentration. The diffusional transport and sorption behavior of Cu(I) and Cu(II) are also separately incorporated.

INTRODUCTION

Copper is considered for a long-term canister material because 1) copper displays an extensive range of thermodynamic stability over mildly reducing, mildly alkaline conditions expected in a deep, crystalline-rock repository, and 2) for redox conditions outside of this range of stability, the rate of formation of more stable copper solids can be constrained by rate of diffusive mass-transport of reactants (or products) through the compacted bentonite buffer. Diffusive transport rates are highly predictable compared to other long-term processes that may affect near-field performance, and can be used to set upper limits on the rates of general corrosion of metallic copper canisters [1].

CAMEO is a performance assessment code developed to evaluate the rate of general corrosion of copper canisters constrained by diffusive mass-transport, and to estimate containment failure times over a wide range of postulated repository conditions. CAMEO is modified from the CALIBRE code, previously developed for and tested by the Swedish Nuclear Power Inspectorate (SKI) for source-term analysis of radionuclide release from the engineered barriers. The computational structure and capabilities of CAMEO are presented. Note, that while general corrosion is often postulated to control the long-term performance of copper canisters [1], potential localized corrosion mechanisms must also be considered in a complete assessment.

MASS-TRANSFER LIMITS TO GENERAL CORROSION

The near field of a deep geological repository for spent nuclear fuel is illustrated in Figure 1. The spent fuel is shown as contained within a copper canister located within an excavation hole or drift. This waste package is surrounded by a low permeability buffer material, typically compacted bentonite or bentonite-sand mixture. The low permeability of the buffer prevents advective flow of water through it, effectively decoupling the waste package from the hydrology of the site. The migration of reactants and products across this buffer are constrained by diffusive mass-transport, which is inherently more predictable over long time scales ($>10^3$ years) than are estimates of future repository flow conditions and corrosion kinetics.

Mat. Res. Soc. Symp. Proc. Vol. 353 © 1995 Materials Research Society

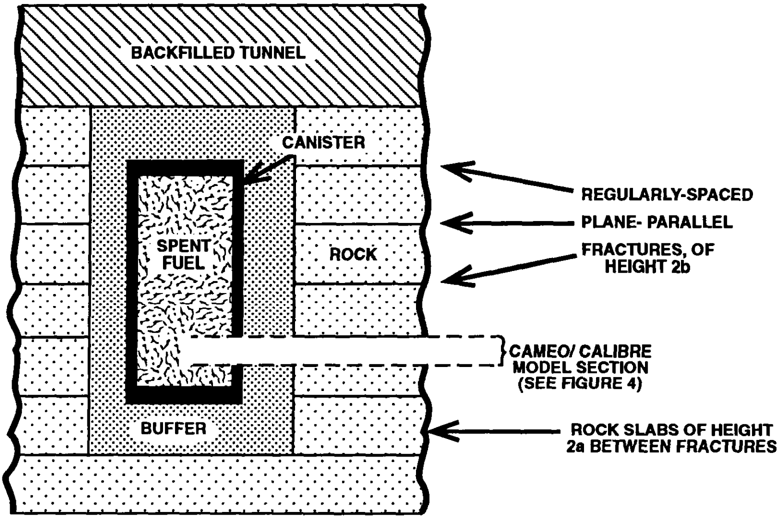


Figure 1 Conceptual Model of the Near-Field of a Spent Fuel Repository

General corrosion of copper is assumed to be constrained by diffusive mass-transport rates of reactants to the canister surface, or reactants away from this surface. Three limiting models are identified, and conceptual models for each are briefly described in the following sections:

1. Sulfide transport to the canister surface under reducing conditions [1,2].
2. Oxygen transport to the surface under mildly oxidizing conditions [3,4].
3. Copper chloride transport away from the surface under highly oxidizing conditions [3,4].

The rates of interfacial attachment/ detachment reactions (i.e., corrosion kinetics) at the canister surface could, under certain circumstances, further limit the rate of general corrosion [4]. Also, formation of corrosion-product layers might impede the transport of reactants to, or products from, the canister surface. In robust safety assessments such effects are typically disregarded as unnecessary for a conservatively defensible estimate of the canister lifetime. Other assumptions are made in analysis of general corrosion controlled by diffusive mass transport, especially the assumption that reactants uniformly reach and are consumed at the canister surface [5].

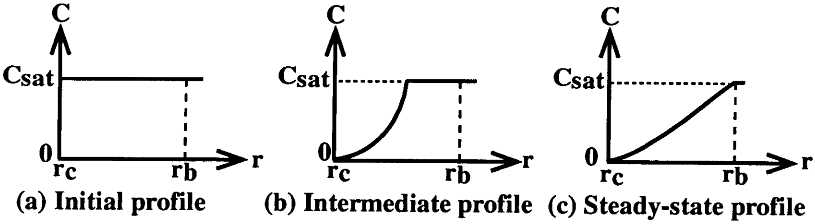
GENERAL CORROSION OF COPPER UNDER REDUCING CONDITIONS

Under sufficiently redox conditions and in the presence of sulphide, copper sulphides (or copper-iron sulphides) become more stable than copper. The long-term general corrosion rate of copper canisters equals, therefore, the mass-transport rate of dissolved sulphide (or total dissolved sulphur species) through the bentonite buffer to the canister surface [1, 2]. The chemical reaction of copper metal, Cu°, can be written as:

$$2Cu^{\circ} + HS^{-} + H_2O \rightleftarrows Cu_2S + H_2 + OH^{-} \qquad (1)$$

Each mole of aqueous sulphide species (HS^-) that arrives at the copper surface is assumed to react with two moles of copper to form chalcocite, Cu_2S. While other stoichiometric copper sulphides are possible, chalcocite conservatively represents the highest ratio of moles of copper consumed by corrosion per mole of sulphide. Instantaneous reaction is assumed, so that no credit is taken for reaction kinetics between copper and aqueous sulphide species.

There are several potential sources of dissolved sulphide. The closest source is the disseminated iron sulphides occurring as a minor phase within the bentonite. These distributed sulphides acts to locally buffer the concentration of dissolved aqueous sulphide species at the solubility value for the iron sulphide (c_{sat}, Figure 2a). As dissolved sulphide is consumed in the general corrosion of copper, the iron sulphides continue to dissolve until completely consumed, and the local concentration of dissolved sulphide decreases to zero. Iron sulphides closest to the canister (at r_c) are consumed first. A steady-state concentration profile for dissolved sulphide develops (Figures 2b and 2c), with c_{sat} fixed at the buffer-host rock interface (r_b). The rate this profile develops is controlled by the amount of sulphides in the buffer.



(a) Initial profile (b) Intermediate profile (c) Steady-state profile

Figure 2. **Evolution of Sulphide Concentration in Buffer Arising from Local Dissolution of Disseminated Iron Sulphides.**

Also important for the long-term general corrosion rate of copper canisters is the concentration of sulphide at the buffer-rock interface. This concentration is typically assumed to be fixed over time because the rate of replenishment by advective transport in the rock is expected to be much greater than the rate of diffusive transport of sulphide into the buffer. The concentration of dissolved sulphide at the buffer-rock interface is considered to be controlled by dissolution of iron sulphide minerals occurring as minor phases in the rock. Dissolved sulphate and sulphate minerals in bentonite represent additional potential sources of reduced sulphur. This would require microbiological reduction of sulphate, a topic outside the scope of this present paper.

Pits may form in the canister and may penetrate the canister sooner than the assumed general corrosion of the copper. Empirical pitting factors (i.e., the aspect ratio of the depth of such pits to the depth of general corrosion, typically a value of 2 to 5) are applied to describe if and when a pit may lead to initial penetration, hence failure, of the canister.

GENERAL CORROSION OF COPPER UNDER OXIDIZING CONDITIONS

With increasing oxidizing conditions in a repository, cuprite (Cu_2O) becomes more stable than copper. At even more oxidizing conditions, tenorite (CuO) becomes more stable than cuprite. For extremely high amounts of dissolved chloride under mildly to strongly oxidizing conditions, it is possible that various copper chlorides and mixed chloride-oxyhyroxides may be more stable that the corresponding pure oxides of copper.

The overall interfacial reaction (both cathodic and anodic processes) for copper dissolution under oxidizing conditions can be expressed as:

$$Cu^{o} + H^{+} + \tfrac{1}{4}O_2(aq) + 2Cl^{-} \rightleftarrows CuCl_2^{-} + \tfrac{1}{2}H_2O \qquad (2)$$

The log of the equilibrium constant for this reaction at STP is 16.84 [6]. Interfacial attachment/detachment rates are observed to be faster than diffusive rates of reactants to, or products away from, the canister surface [4]. Accordingly, corrosion kinetics of copper are typically dismissed as unnecessary for conducting a conservative analysis of containment. The long-term general corrosion rate under oxidizing conditions is constrained, therefore, either by the transport rate of oxygen (or oxidant) to the canister surface, or by the transport rate of dissolved copper chloride away from canister surface.

These transport rates, especially for dissolved copper chloride, can be impacted by additional chemical processes (Figure 3), such as precipitation of new copper phases, oxidation of dissolved copper species (Cu(I) → Cu(II)), and adsorption of Cu(I) and Cu(II) species on bentonite. Conceptual models for these two rate-limiting processes are described below.

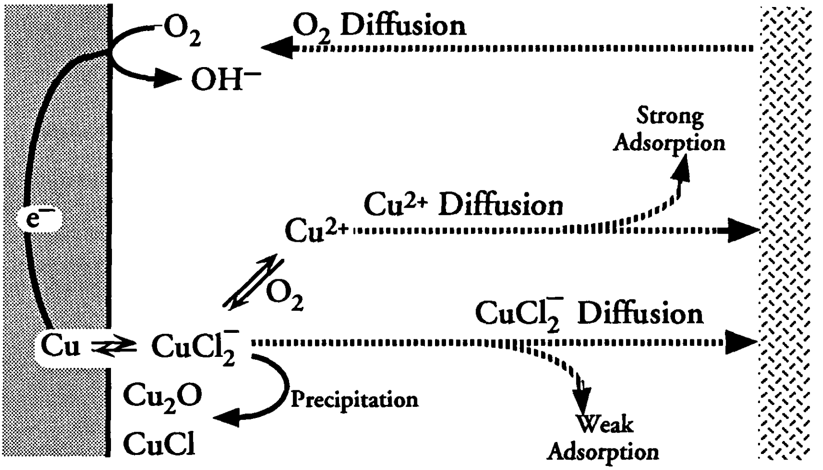


Figure 3. Schematic of Chemical and Transport Processes Affecting General, Uniform Corrosion of Copper Canisters under Oxidizing Conditions (after references [3, 4]).

Corrosion Limited by Oxygen-Transport Rate

For mildly oxidizing conditions, the rate that dissolved oxygen reaches the canister surface limits the general corrosion rate of copper canisters. Four moles of copper are consumed by general corrosion for each mole of dissolved oxygen that diffuses to the canister surface (eqn. 2).

The oxygen transport rate through the buffer is governed by the oxygen partial pressure in groundwater at the buffer-rock interface. This may be as low as 10^{-50} bars that is required for incipient formation of cuprite, Cu_2O from copper metal [7], and it certainly can be higher. The oxygen concentration at the buffer-rock interface is assumed to be fixed by advective transport of oxygen concentration at the buffer-rock interface is assumed to be fixed by advective transport of oxygen to this interface. All of the oxygen that diffuses through the buffer and reaches the canister surface is assumed to be consumed, so the inner boundary condition for the concentration of oxygen is zero. No credit is taken for the rate of copper corrosion by oxygen or any affects arising from potentially protective or passivating layers of corrosion products, such as Cu_2O, that may form on the canister. The structure and assumptions for this oxygen-transport model are similar to the conceptual model for sulphide transport under reducing conditions.

Primary sources of oxygen to drive this postulated general corrosion reaction are 1) oxygen introduced and trapped in engineered materials (e.g., buffer and tunnel backfill) and rock during the construction and emplacement of the nuclear waste repository, or 2) deep circulation of oxygenated groundwater, which might arise from glaciation, changes in sea level, reactivation of faulting, etc. For this latter scenario, it is not only the concentration of oxygen that is important but also the duration of the circulation. As with the sulphide case, the long-term, general corrosion by oxygen is determined by magnitude of the chemical concentration gradient, that is proportional to the concentration of oxygen at the buffer-rock interface.

Corrosion Limited by Copper Chloride-Transport Rate

With increasing oxygen concentration at the buffer-rock interface, the general corrosion rate of copper canisters eventually ceases to be limited by the transport rate of oxygen *to* the canister surface. Instead, corrosion rate is determined by the diffusional-transport rate of reaction products, assumed to be dissolved copper chloride ($CuCl_2^-$), *away* from the canister surface (Figure 3). To determine this rate, the concentration of the copper chloride species ($CuCl_2^-$) at the canister surface and at the buffer-rock interface must be known or calculated.

The maximum concentration of $CuCl_2^-$ at the canister surface is set by the equilibrium solubility of copper at the highly oxidizing Eh value assumed to be imposed at the buffer-rock interface. Copper is not the most thermodynamically stable phase under such highly oxidizing conditions. Even if more stable copper-bearing phases form at the canister surface, however, the corrosion rate of the copper canister itself is assumed to be driven by the equilibrium solubility of metastable copper. Other workers [4] have suggested that a mixed-potential, kinetic rate constrains the boundary concentration for $CuCl_2^-$ at the copper surface under such conditions.

The interfacial concentration of $CuCl_2^-$ is assumed to be constrained by the solubility of copper metal, $C_{sat}^{Cu^\circ}$. This can be calculated using the equilibrium constant cited for reaction (2):

$$10^{16.84} = \frac{[CuCl_2^-]}{[H^+]P_{O_2}^{0.25}[Cl^-]^2} \qquad (3)$$

$$C_{sat}^{Cu^\circ} = [CuCl_2^-] = 10^{16.84}[H^+]P_{O_2}^{0.25}[Cl^-]^2 \qquad (4)$$

$$= 10^{16.84}10^{-pH}P_{O_2}^{0.25}[Cl^-]^2 \qquad (5)$$

$$= 10^{-4.01}10^{16.95Eh}[Cl^-]^2 \qquad (6)$$

Bracketed terms are in moles/liter, the partial pressure of O_2, P_{O_2}, is in bars and Eh is in volts.

For the outer boundary condition, advective transport in the rock is expected to be relatively rapid compared to diffusive transport in the buffer. Accordingly, the concentration of $CuCl_2^-$ at the buffer-rock interface is conservatively set to zero (i.e., a swept away boundary condition).

The net rate of transport of $CuCl_2^-$ through buffer can be further impacted by oxidation of dissolved copper species from Cu(I) to Cu(II) [8]. Initial corrosion/dissolution of copper metal produces Cu(I) species, even under highly oxidizing conditions [4]. Furthermore, the diffusion of $CuCl_2^-$ as the rate limiting step for general corrosion of copper can only be expected under strongly oxidizing conditions [3, 4]. It likely, therefore, that the initially released Cu(I) species are further oxidized to Cu(II) species during transport through the buffer. This oxidation mat affect the copper corrosion rate because anionic Cu(I) species are only weakly adsorbed by bentonite, while cationic Cu(II) species are strongly sorbed. Strong adsorption locally decreases the dissolved concentration of copper, locally steepening the concentration gradient, hence enhancing the diffusive transport rate of copper away from the surface of the copper canister.

DESCRIPTION OF THE CAMEO/ CALIBRE CODES

The previously described conceptual models for diffusive mass-transport control of general corrosion of copper canisters have been implemented into the CAMEO code. CAMEO is adapted from the finite-difference CALIBRE code [9], originally developed for the SKI to evaluate mass-transfer limited release of radionuclides from the near field [2].

The section of the canister and near field modelled in CAMEO is illustrated in Figure 4. The fractured rock is idealized, such that the fractures occur in the horizontal plane, are plane-parallel and spaced at regular interval. This idealization allows the CAMEO model to take advantage of the symmetry of such a system. The inner Z-axis shown corresponds to the vertical axis of the cylindrical canister, while the r-axis is the radial direction.

For the oxygen and sulphide corrodant cases, the near-field components include only the copper canister and buffer, with a constant concentration of these reactive species assumed at the bentonite-rock interface. For the sulphide case, uniformly distributed iron-sulphide solids can be modeled as part of the bentonite backfill that additionally contribute reactive sulphide species.

The corrosion model for diffusive transport of $CuCl_2^-$ away from the canister surface includes fractured rock that could enhance the flux of $CuCl_2^-$ away from the canister. CAMEO employs either a chemical-equilibrium model (as a function of pH, Eh, and [Cl^-]) or a mixed-potential model for estimating the canister corrosion rate and surficial concentration of $CuCl_2^-$. A kinetic model [8] for Cu(I) oxidation to Cu(II), also as a function of pH, Eh, and [Cl^-], is implemented in CAMEO. Different sorption parameters can also assigned to Cu(I) and Cu(II) species.

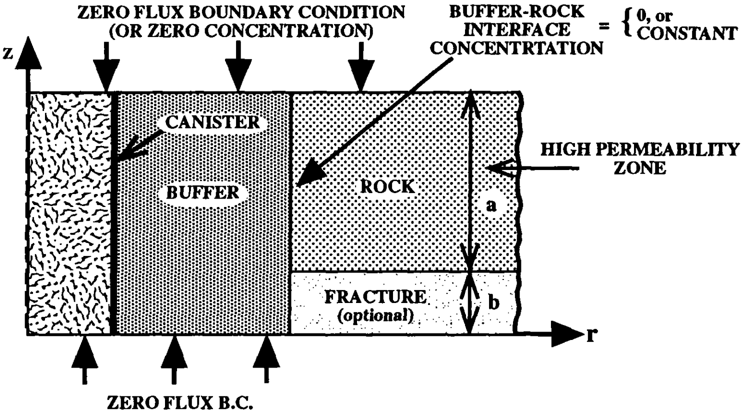


Figure 4. Section of the Near-Field Modelled in CAMEO (with Canister No Spent Fuel) and CALIBRE (with Spent Fuel, No Canister).

The transport equations in CAMEO are solved by approximating the differential equations by difference equations in time and space. The ratio of total mass concentration to dissolved concentration for each species is assumed to remain constant over a timestep, to avoid the solution of non-linear equations. Errors introduced by these approximations are minimized by employing an adaptive time-stepping algorithm. The algorithm imposes small steps during periods of rapidly changing conditions, and larger ones as the system approaches steady-state.

PRELIMINARY CAMEO CALCULATIONS

A series of CAMEO calculations are presented in Tables I to III for steady-state general corrosion of a 0.06-meter thick ACP copper canister [5]. An unlimited, uninterrupted supply of all reactants diffusing across a 0.35-meter thick buffer. A standard pitting factor of 5 is adopted.

Table I shows steady-state corrosion rates and times to canister failure for reducing conditions. It can be seen that the canister lifetime for disposal is on the order of many millions of years under normally postulated reducing conditions, even with pitting taken into account. Sulphide originating as minor phases in the bentonite buffer has a negligible effect on this prediction (¶ in Table I). For a postulated scenario of dissolved sulphate diffusing in through the buffer, undergoing reduction (possibly microbially mediated), and reaction with copper (‡ in Table I), a significantly shorter canister lifetime is predicted, on the order of tens of thousands of years.

Table II shows that for the air-saturated groundwaters, the predicted time to canister failure is 780,000 years. The conditions leading to deep circulation of such oxidizing waters are speculative, and it is doubtful that such conditions would persist for time periods approaching this duration. Less oxidizing waters lead to extremely long predicted times to canister failure.

Table I. Results for General Corrosion Controlled by Diffusive Transport of Dissolved Sulfur Species.

Concentration at Rock-Buffer Interface (mol/m^3)	Steady-State Corrosion Rate (mol/yr)	Time to Failure by General Corrosion (10^6 yr)	Time to Failure by Pitting Corrosion (10^6 yr)
$[S^{2-}] = 3.2 \times 10^{-2}$	3.9×10^{-4}	26.	6.7
$[S^{2-}] = 3.2 \times 10^{-2}$¶	3.9×10^{-4}	26.	6.7
$[SO_4^{2-}] = 2.1 \times 10^{1}$‡	2.6×10^{-1}	0.039	0.010
$[SO_4^{2-}] = 2.1 \times 10^{1}$¶‡	2.6×10^{-1}	0.039	0.010

Table II. Results for General Corrosion Controlled by Diffusive Transport of Dissolved Oxygen.

O_2 Concentration at Rock-Buffer Interface (mol/m^3)	Steady-State Corrosion Rate (mol/yr)	Time to Failure by General Corrosion (10^6 yr)	Time to Failure by Pitting Corrosion (10^6 yr)
5×10^{-1}	1.3×10^{-2}	0.78	0.20
5×10^{-4}	1.3×10^{-5}	780	200
5×10^{-7}	1.3×10^{-8}	» 10^9	» 10^9

Table III. Results for General Corrosion Controlled by Diffusive Transport of Copper Chloride.

Eh (V) at Canister Surface	[Cl-] (mol/m^3)	Steady-State Corrosion Rate (mol/year)	Failure Time for General Corrosion (Years)	Failure Time for Pitting Corrosion (Years)
0.4	10	3.7×10^{-1}	2.7×10^4	5.7×10^3
0.0	0.1	6.1×10^{-12}	» 10^9	» 10^9
0.0	10	6.1×10^{-8}	» 10^9	» 10^9
0.0	1000	6.1×10^{-4}	1.6×10^7	3.4×10^6

Table III presents sensitivity results for the case of diffusion of $CuCl_2^-$, confirming that the steady-state corrosion rate is proportional [$CuCl_2^-$] (i.e., the square of [Cl–], see eqn. 6). It also shows that unless the Eh at the copper canister surface is extremely oxidizing, the predicted containment times are well in excess of 10^6 years. Indeed, it is only under the most oxidizing conditions, with an abundant supply of O_2, that the diffusive transport of $CuCl_2^-$ (rather than O_2) will become the rate-determining step for the general corrosion of copper canisters.

ACKNOWLEDGEMENTS

This work has been conducted through funding by the Swedish Power Nuclear Inspectorate, SKI, for which we are grateful. In implementing the CAMEO code, we have greatly benefitted from research by, and discussions with, Dr. F. King and associates at the Atomic Energy of Canada, Limited. We thank them for their willingness to selflessly share their ideas and results. Any errors or misstatements in this paper are, however, entirely the authors' responsibility.

REFERENCES

1. SKB, (1992), SKB-91. Final Disposal of Spent Nuclear Fuel. Importance of the Bedrock for Safety. SKB Technical Report 92-20, SKB, Stockholm, Sweden.
2. SKI (1991), SKI Project-90, SKI Technical Report 91-23, Summary, Vols. I and II, August 1991, Swedish Nuclear Power Inspectorate, Stockholm, Sweden.
3. King, F. and D. LeNeveu, (1992), "Prediction of the lifetimes of copper nuclear waste containers," Focus '91, Am. Nuc.Soc., LaGrange Park, IL, pp. 253-261.
4. King, F., D. M. LeNeveu and D. J. Jobe, (1993), "Modelling the effects of evolving redox conditions on the corrosion of copper containers," Scientific Basis for Nuclear Waste Management XVII, Materials Research Society, Pittsburgh, PA.
5. Werme, L., (1990), Near-field Performance of the Advanced Cold Process (ACP) Canister, SKB Technical Report 90-31, SKB, Stockholm, Sweden.
6. Helgeson, H. C., J. M. Delany, H. W. Nesbitt, and D.K. Bird, (1979), "Summary and critique of the thermodynamic properties of rock-forming minerals," Am. J. Sci., 278A, 229.
7. SKN, (1992), Stability of Metallic Copper in the Near Surface Environment, SKN Report 57, National Board for Spent Nuclear Fuel, Stockholm Sweden.
8. Eary, L. E. and J. A. Schramke, (1990), "Rates of inorganic oxidation reactions involving dissolved oxygen," Chemical Modelling of Aqueous Systems II, Am. Chem. Soc., NY, NY.
9. Worgan, K. and P. Robinson, (1993), The CALIBRE Source Term Code: Technical Documentation for Version 2, Intera Information Technologies Report No.: IM3583-3, 1993.