PROCEEDINGS, Tenth Workshop on Geothermal Reservoir Engineering
Stanford University, Stanford, California, January 22-24, 1985
SGP-TR-84

CO_2 TRENDS IN THE DEPLETION OF THE LARDERELLO VAPOR-DUM1NATED RESERVOIR

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Introduction

Most Larderello wells produce superheated stem, with a noncondensible gas content of 3–10 percent by weight, of which typically 95 percent consists of CO_2 (D'Amore and Truesdell, 1984). For most wells for which long-term depletion data are available the gas content of the discharge shows remarkably small temporal variations. In many cases the gas-steam ratio changes by no more than 10 to 20 percent over several decades, and there are only few wells where gas content changes by as much as s factor of 3, which is still a rather modest change. In many wells there is a tendency for gas content to increase for several years, then stabilize, and eventually decrease (Sestini, 1970; D'Amore and Truesdell, 1979; Calore et al., 1982).

The present paper is concerned with the origin of CO_2 in the Larderello discharges from a reservoir engineering point of view. Specifically, we consider the question of fluid reserves (water and CO_2) at Larderello, and we carry out numerical simulations to obtain insight into temporal trends of CO_2 released from idealized models of vapor-dominated systems. Important constraints in the modeling arise from observed temperatures and enthalpies at Larderello. Discharge enthalpies are generally close to those of saturated steam near 250°C (2.8 MJ/kg), with some degree of superheat which tends to increase with time. Flow rates of most wells decrease rapidly during the first few years of production and subsequently decline very slowly (Sestini, 1970; Weres et al., 1977; D'Amore and Truesdell, 1979).

Fluid Reserves

Total cunulative fluid production from the Larderello reservoir is large. Extrapolating data given by Sestini (1970) we estimate that approximately 400×10^9 kg of fluid have been extracted to date from the central zone of Larderello, which covers an area of approximately 20 km^2. On the basis of this large cumulative production, it has been concluded by several authors that moat of the fluid reserves were originally in place in liquid form, because storage of such fluid quantities in vapor form would require an unreasonably large reservoir thickness (James, 1968; Nathenson, 1975; Weres et al., 1977). In order to calculate specific fluid depletion (i.e., mass of fluid extracted per unit reservoir volume), it is necessary to estimate the average thickness of the productive formations, and to allow for the fact that total drainage area will be larger than the well field area. Adopting a value $h = 1$ km for reservoir thickness, and taking a conservative factor 2 for reservoir volume to account for production from greater depth, or from outside the drilled area, we obtain a specific depletion to date of approximately 10 kg/m^3. For an estimated porosity of ≤ 5 percent, the vapor in plact is ≤ 1 kg/m^3 (for a vapor density of $\rho_v \approx 20$ kg/m^3 at 250°C). If 10 kg/m^3 of fluid are extracted from boiling liquid (with a density of $\rho_\ell \approx 800$ kg/m^3 at 250°C), then the corresponding decrease in liquid saturation is $\Delta S_\ell = 0.25$. From these conaidbrations we conclude that initial (pre-exploitation) liquid saturation in the Larderello resetvoir has to have been no less than $S_\ell = 0.25$.

Let us now turn to the question of CO_2 reserves. The average CO_2 content of the fluids produced in Larderello is $X_c = 5$ percent by mass, with most individual wells falling in the range of $3\% \leq X_c \leq 10\%$. Could the produced CO_2 have been stored in the original reservoir fluid? In Figure 1 we have plotted CO_2 masa fractions of two-phase mixtures as a function of liquid saturation, with CO_2 partial pressure P_c as parameter (temperature 250°C). It is seen that for a given partial pressure of CO_2, the CO_2 content of two-phase fluid decreases rapidly with increasing liquid saturation. The effects are temperature dependent. If temperature is increased the CO_2 content of the vapor phase diminishes, while that of the liquid phase increases. At intermediate saturations $0.2 \leq S_\ell \leq 0.5$ these phase distribution effects tend to cancel out, so that CO_2 content is determined mostly by partial pressure, with little temperature dependence. For the lowest value of liquid saturation which is compatible with cunulative fluid production to date, $S_\ell = 0.25$, an average CO_2 content of $X_c = 5$ percent requires a CO_2 partial pressure of $P_c \approx 15$ bars. Such partial pressures are inconsistent with field measurements of pressures and temperatures at Larderello. Indeed, in zones which had not been heavily exploited the observed temperatures and pressures correspond rather closely to the saturated vapor pressure curve for water, $P_v \approx P_{sat}(T)$, indicating that CO_2

partial pressure is small (perhaps P_c = 1-2 bars). From this we conclude that only a small fraction of the produced CO_2 at Larderello could have been originally stored in the reservoir fluids. Most of the produced CO_2 has to have been supplied either by an external source (presumably located at greater depth), or by an internal source (**i.e.**, a mineral buffer).

Numerical Simulations

The conclusion reached above about the origin of CO_2 in Larderello discharges is supported by results of numerical simulations. The simulations demonstrate conclusively that CO_2 concentrations and trends in produced fluids can not be explained in terms of CO_2 content in place in the original reservoir fluids. Before discussing the numerical results it is appropriate to describe the general pattern of C02 concentration change expected from two-phase flow and phase change phenomena.

For temperature and pressure conditions relevant to vapor-dominated systems, the amount of CO_2 present in a unit volume of gas phase is larger by a factor of about 3 than the mount dissolved in a unit volume of liquid phase (see Figure 2). After depletion of a block of porous rock is initiated, the liquid saturation generally tends to decrease because of boiling. This enhances gas phase mobility (relative permeability), causing CO_2 concentrations in the fluids discharged from rock matrix blocks to rise. However, the boiling liquid is less rich in CO_2 than the initial gas phase, so that CO_2 concentrations in the gas phase decline during depletion. This effect slows down the increase in discharged CO_2 concentrations brought about by enhanced gas mobility, and eventually reverses the trend, causing discharged CO_2 concentrations to decline. Therefore, the combination of two-phase flow and phase change effects is expected to yield CO_2 trends compatible with field observations for many Larderello wells: an initial period of increasing CO_2 concentrations, followed by a period of approximately constant composition, and an eventual decline in C02 concentrations.

The general trends described above are borne out by nunerical simulations. We have used the H_2O/CO_2 version of Lawrence Berkeley Laboratory's general purpose simulator MULKOM (Pruess, 1983a; O'Sullivan et al., 1983) to study fluid discharges from porous matrix blocks of low permeability. The simulations were made with the method of multiple interacting continua (MINC; Pruess and Narasimhan, 1982), and different levels of space discretization were used to verify that spatial truncation errors were negligible. Figure 3 shows simulated CO_2 transients for fluid discharge from a porous cube of 50 m side length with parameters given in Table 1. At the production rate specified, total block depletion takes 51.9 years. CO_2 concentrations increase by almost a factor of 3 for the first five years, and subsequently decline, as expected. Comparing these results with typical field data for Larderello wells, it is apparent that the simulated changes in CO_2 concentrations are stronger and occur more rapidly than are generally observed in the field. We do not consider this a serious shortcoming of the simulation. Observed CO_2 concentrations in the field represent an average of fluid discharges from many matrix blocks. As the drainage volume of a well expands with time, matrix blocks at greater distance from the well will contribute increasing CO_2 concentrations, while matrix blocks near the well will discharge fluids of declining CO_2 content. The superposition of these effects is expected to diminish and slow dorm CO_2 concentration dhanges in comparison to the single block response shown in Figure 3, giving a response more compatible with field data.

A more serious problem with the simulated CO_2 trends is the absolute magnitude of CO_2 mass fraction, which is smaller than typical field values by a factor of 20-301. In the simulation we used a CO_2 partial pressure of 1 bar. In order to obtain CO_2 mass fractions in the range of 5-8 percent, as obsarved in the field, we would require unreasonably large partial pressures. Alternatively, we could modify relative permeability parameters, or in-place liquid saturations, to enhance gas phase flow in comparison to liauid flow in the matrix. (For the conditions chosen in the simulation, the gas phase contains initially apprbximately 5 percent CO_2 by mass.) However, this gives rise to other problems, which are discussed below.

The most serious failure of the simulation occurs with regard to flowing enthalpy. Figure 3 shows that initial discharge enthalpy is as low as 1.07 MJ/kg. Approximately 6 years of discharge are required before enthalpy appaoaches a value of 2.8 MJ/kg which is compatible with field obervations. This enthalpy behavior was not anticipated. Rather, we had expected that because of the low matrix block permeability a strong conductive enhancement of flowing enthalpy would take place, so that superheated vapor would be discharged even as liquid is mobile and flowing in the matrix (Pruess, 1983b). Interestingly, however, the presence of CO_2 suppresses the mechanism of enthalpy enhancement described by Pruess (1983b). As discharge from the matrix block is initiated, a gradient in CO_2 partial pressure is established inside the matrix block, which is entirely sufficient to drive mass flux at the desired rate of fluid discharge. For a period of several years the gradient of vapor pressure remains negligibly small in comparison to the gradient of CO_2 partial pressure. Therefore, temperature gradients inside the matrix block are also very small, and conductive enhancement of flowing enthalpy is negligible.

The only way to obtain discharge enthalpies near 2.8 MJ/kg is to adjust parameters in such a way that liquid is immobile in the matrix. However, in simulations with immobile liquid we invariably obtain a rapid decline of CO_2 concentrations with time, caused by dilution of the gas phase from boiling liquid. Over the time period required to deplete the original gas phase in place, CO_2 concentrations decline by a factor of approximately 30.

The conclusion from these simulation studies confirms the result from the analysis of fluid reserves, above. Namely, the concentration and trends of CO_2 in Larderello discharges can not be explained by assuming that produced CO_2 originates from the reservoir fluid.

Mineral Buffer for CO_2

The discussion of fluid reserves and the nunerical simulation results given above indicate that most of the C02 produced at Larderello originates either from external or from internal (mineral buffer) sources. We consider the external source hypothesis (CO_2 supplied from beneath the main reservoir) to be rather improbable. Observed temporal variations in CO_2 content of discharges are generally small over several decades, while flow rates of individual wells often change by sn order of magnitude or more. The relative constancy of CO_2 content would be difficult to explain in a model with external source, while it follows naturally when a mineral buffer is assumed.

Several authors have suggested that noncondensible gas concentrations in geothermal reservoirs, and in particular CO_2 partial pressures, are controlled by equilibriun reactions involving mineral assemblages (Giggenbach, 1981; Cavarretta et al., 1982; Arnorsson et al., 1983; Giggenbach, 1984). Cavarretta et al. (1982) showed that the CO_2 partial pressures at Larderello and Serrazzano are close to equilibrium for the reaction

$$\text{2 clinozoisite} + \text{3 quartz} + \text{2 calcite} = \text{3 prehnite} + 2\,CO_2 \qquad (1)$$

Following these authors we have considered a depletion model with a mineral buffer as given by Equation (1). Very little is known about the kinetic rates of reactions such as (1). We have adopted a first order rate law ad hoc, assuming that the volumetric rate of CO_2 release from minerals is proportional to the difference between equilibrium and actual partial pressure of CO_2:

$$q_{CO_2} = \alpha\,(P_c^{eq} - P_c) \qquad (2)$$

An internal CO_2 source as given by Equation (2) was incorporated into the MULKOM simulator. It is believed that the mineral buffer reaction Equation (1) can only proceed in the presence of liquid water. Therefore, the rate constant α should go to zero for $S_\ell \to 0$. This is taken into account in our simulations by replacing $\alpha \to \alpha \cdot S_\ell/0.05$ for $S_\ell < 0.05$. The temperature dependence of P_c^{eq} is expressed by an empirical fit to data for the reaction (1), which were provided to us by Gianelli (private communication, 1984). The relationship is:

$$\log P_c^{eq} = 1.437 \times 10^{-2}\,T - 1.4 \times 10^{-5}\,T^2 - 2.81 \qquad (3)$$

Reaction (1) and Equation (3) are considered valid in the 250-350°C temperature range and for the deeper layers of the reservoir (metamorphic basement) of Larderello. Lacking more detailed information on possible mineral buffers in different parts of the reservoir and in different temperature ranges, at present we have assumed that a relationship like Equation (3) could be considered valid for the entire reservoir and in a wider temperature range ($200°C < T < 350°C$).

It is interesting to note that over the temperature interval $200°C \leq T \leq 300°C$ the ratio of equilibriun partial pressure of CO_2, as predicted by Equation (3), to the saturated vapor pressure is practically codstant. We have

$$\frac{P_c^{eq}(T)}{P_{sat}(T)} = 0.0204 \pm 0.61 \qquad (4)$$

From this it follows that equilibriun CO_2 mass fractions in vapor are independent of temperature (for $200°C \leq T \leq 300°C$), if in fact CO_2 partial pressure is controlled by the reaction (1).

Using the above model of a finite rate mineral buffer, we have simulated the depletion of individual matrix blocks. In the simulations it was necessary to limit time steps to a modest saturation change per time step, because of the dependence of buffer rate upon liquid saturation. Simulation results should be considered illustrative of mechanisms rather than quantitative, because of the uncertainties involved in the parameters for the mineral buffer.

Simlation of block depletion with mineral buffer was performed with the same parameters as in Table 1, except for initial P_c, which was assuned equal to the equilibrium value at 240°C (0.6798×10^5 Pa). Binary diffusion was also included in the simulations. A diffusiviy at standard conditions (0°C, 1 atm.) of $D_s = 1.38 \times 10^{-5}$ m^2/s and a temperature and pressure dependence of the type

$$D(T,P) = D_s \frac{P_s}{P} \left(\frac{T}{T_s}\right)^{1.91}$$

with T = absolute temperature, were assumed (Perry, 1963).

Some results for simulated block depletion are shown in Figure 4. The four curves correspond to different values of the rate constant a of Equation (2).

For high values of a [$10^{-10} - 10^{-12}$ kg/($m^3 \cdot s \cdot Pa$)], the CO_2 content in the produced fluid, after an initisl transient, reaches valuers which are comparable with those observed in the field, but the CO_2 fraction remains practically constant up to the complete depletion of the block. With lower a values we obtain a trend more similar to that observed in many Larderello wells, but the maximum values are significantly lower than in the field.

Enthalpy rises faster than in the case without mineral buffer, and the more rapid increases are obtained with higher values of a. This is due to the fact that CO_2 generation tends to reduce P_c-gradient, so that conductive enthalpy enhancement is stronger. Diffusion also contributes to reduce the P_c gradient.

The initial values of CO_2 concentration and enthalpy appear still too low in comparison with real data due to the initial liquid flow out of the block, which in these simulations is relatively high, an initial liquid saturation of 0.8 being assumed. Higher initial values of both CO_2 mass fraction and enthalpy are obtained with a lower initial water saturation (Figure 5). Now the CO_2 content of the produced fluid does not show the fast decrease which occurred without mineral buffer. With the initial liquid saturation used in this case *(0.6)* the depletion time is still about 38 years.

Figure **6** shows the cumulative CO_2 mass generation per unit volume as a function of distance from the block surface for the four cases of Figure 4. In all cases the curves are sufficiently smooth, but the cases with higher α require a finer space discretization. The curves show different trends at short distances from the block surface. With a very high a, the strong CO_2 generation tends to maintain everywhere in the two-phase zone a P_c close to the equilibriun value, preventing the propagation of P_c drawdown inside the block. The result is that strong generation rates occur in a narrow zone close to the saturation front only. In such conditions total CO_2 generation depends mainly on the velocity of saturation front displacement. This velocity increases as the front moves away from the block surface, due to the decreasing liquid saturation and the consequent lower liquid flow from the inner most parts of the block. With low a, on the contrary, a significant P_c gradient is established throughout the block and CO_2 generation begins very early also at points distant from the saturation front. CO_2 generation is always diffused over a relatively large volume.

Moving away from the block surface, the period of CO_2 generation increases as drying occurs later, but the average generation rate decreases due to the lower average P_c drawdown. The effect of the increasing period of generation prevails at intermediate distances from the block surface, while the decrease of average generation rate generally prevails in the innermost parts of the block.

Conclusions

Overall mass balance considerations and numerical simulations of reservoir depletion show that only a small fraction of the CO_2 produced in Larderello could have been originally stored in the reservoir fluid. Most of the produced CO_2 was supplied either by an external source, or by an internal source (i.e., a mineral buffer). The latter possibility appears more likely, because of the small temporal variations in CO_2 content of well discharges, even as production rates change by large amounts.

Numerical simulations were performed to study CO_2 discharge from rocks of low permeability, with a temperature-dependent prehnite/clinozoisite mineral buffer. Simulated discharge characteristics were found to be in approximate agreement with typical CO_2 trends observed for Larderello wells. However, observed CO_2 concentrations tend to be somewhat larger than the simulated values, suggesting that additional minerals are participating in buffering CO_2.

Acknowledgements

This work was supported, in part, by the Assistant Secretary for Conservation and Renewable Energy, Office of Renewable Energy, Division of Geothermal Energy and Hydropower Technologies of the U. S. Department of Energy under Contract No. DE-AC03-76SF00098. One of us (K.P.) would like to acknowledge the hospitality and support extended by the Istituto Internazionale Per Le Ricerche Geotermiche, without which this work would not have been possible. We thank Dr. G. Gianelli for making his calculations for the prehnite mineral buffer available to us.

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Table 1: Parameters for Simulation

Matrix	
rock grain density	2500 kg/m^3
rock specific heat	960 $J/Kg^\circ C$
rock heat conductivity	2.8 $W/m^\circ C$
porosity	.05
permeability	10^{-17} m^2
relative permeability	Corey curves $S_{\ell r} = 0.30$ $S_{gr} = 0.05$
Fractures (three perpendicular sets)	
spacing	50 m
Initial Conditions	
temperature	240°C
liquid saturation	0.80
CO_2 partial pressure	10^5 Pa
Discharge	
Constant volumetric rate	2×10^{-8} $kg/s \cdot m^3$

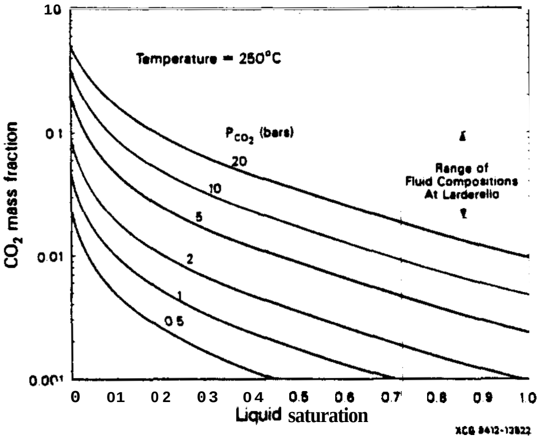

Figure 1. CO_2 mass fraction in two-phase fluid as a function of liquid saturation.

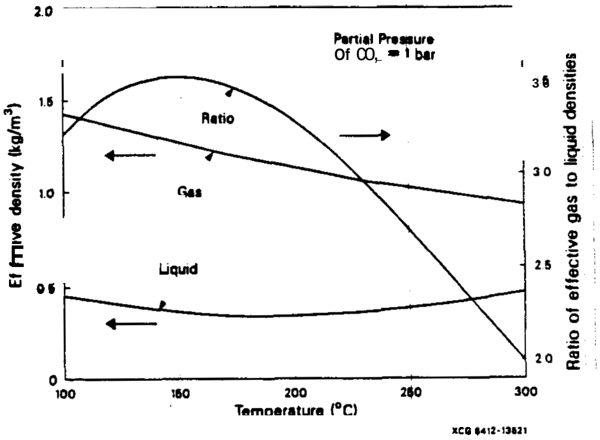

Figure 2. Effective density of CO_2 in gas and liauid phases at a partial pressure of P_c = 1 bar.

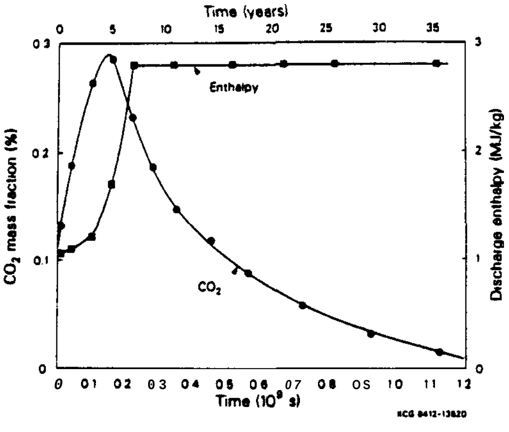

Figure 3. Simulated CO_2 and enthalpy transients for fluid discharge from a porous block of low permeability.

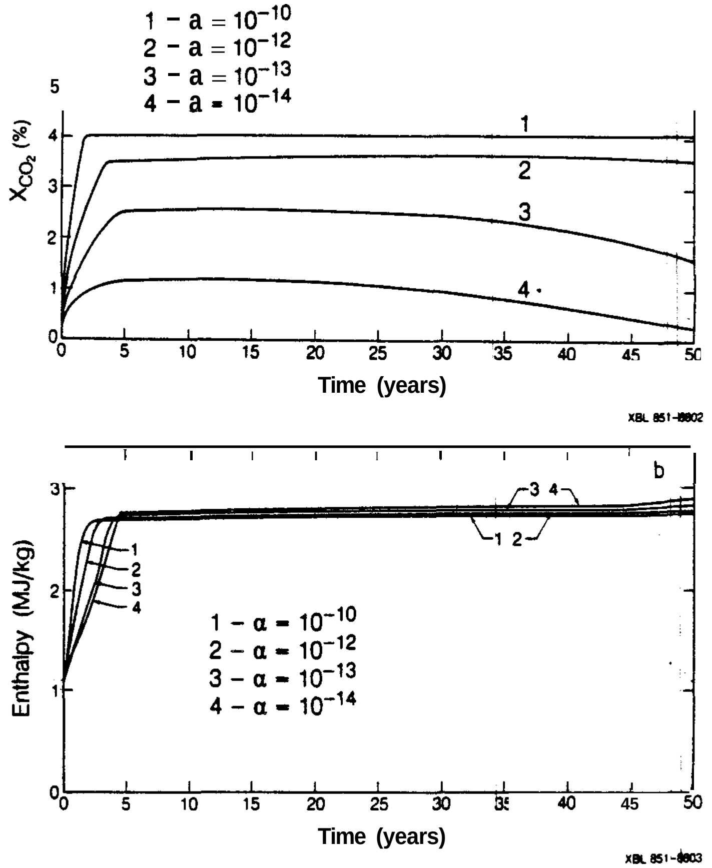

Figure 4. Block depletion model with mineral buffer given by Equation (1). CO_2 mess fractions (a) and enthalpy (b) trends for the discharged fluid. Cases. 1 to 4 with a generation rate constant of 10^{-10}, 10^{-12}, 10^{-13} and 10^{-14} kg/ $(m^3 \cdot s \cdot Pa)$ respectively.

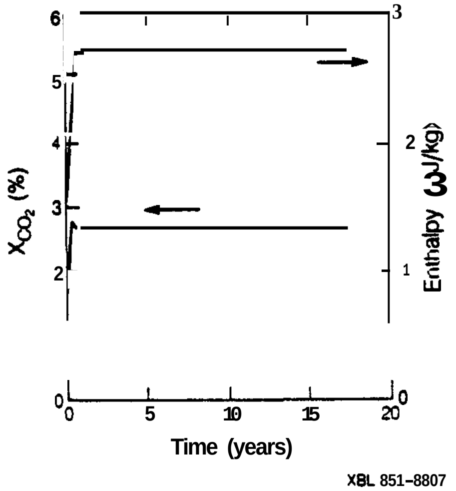

Figure 5. Simulated CO_2 and enthalpy transients for fluid discharge from a porous block with CO_2 internal source and initial liquid saturation of 60%.

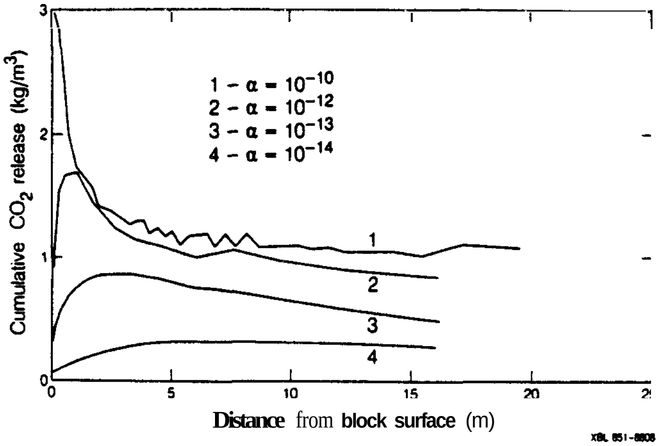

Figure 6. Cumulative CO_2 mass generation per unit volume for the four cases of Figure 4.