Phase Diagram Study of the CaO–CaF₂ System

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Key phase diagram experiments for the CaO–CaF₂ system were conducted using an equilibration and quenching technique and thermal analysis. Equilibration and quenching experiments using sealed Pt capsules followed by FE-SEM EDS compositional analysis and XRD phase analysis were performed to determine the CaO and CaF₂ liquidii and the solubility of CaO in solid CaF₂. Thermal analyses with DSC and TGA were used to determine the temperatures of the eutectic and the α - to β -CaF₂ polymorphic transition. For the first time, noticeable solubility of CaO in α - and β -CaF₂ solids is observed above 1000°C. The maximum solubility of CaO in solid CaF₂ is about 5 mol% at the eutectic temperature (about 1361°C) while no solubility of CaF₂ in solid CaO is detected. Based on the thermodynamic optimization using the present CaO and CaF₂ liquidii and the eutectic temperature measurements, it is concluded that the CaO–CaF₂ binary is a simple eutectic system with the eutectic reaction $L_{(\text{CaO} = 15 \text{ mol}\%)} \rightarrow \text{CaO}_{(\text{pure solid})} + \text{CaF}_{2(\text{solid solution with CaO} = 5 \text{ mol}\%)}$ at 1361°C. The α - to β -CaF₂ polymorphic transition is located at about 1146°C and the melting point of CaF₂ at 1420°C.

KEY WORDS: CaO–CaF₂ system; phase diagram; solubility of CaO in CaF₂.

1. Introduction

Oxy-fluoride systems have been used in various fields such as metallurgy, cement, glass, and refractory industries.¹⁾ In the steelmaking industry, for example, fluorine-containing slag systems are widely used in electro-slag remelting, refining, and continuous casting processes.^{1,2)} In particular, the use of fluorine-containing mould flux plays a critical role in controlling the surface quality of cast products. Since the introduction of the first continuous caster in 1901, the use of continuous casting process in the world has increased a lot in a short period of time and today more than 90% of the steel produced is made by this method.³⁾ Consequently, a deep understanding of fluorine-containing mould flux is very important for the steel industry. Unfortunately, large discrepancies still exist in the experimental data of oxy-fluoride systems. One of the reasons is that oxy-fluoride systems form complex reciprocal systems where both cations and anions can mix together in the liquid state. Moreover, the evaporation of fluorine can change the composition of the charge during the experiment and the fluorine-containing liquid can be hardly quenched.

The CaO–CaF₂ system is one of the most fundamental binary system in the metallurgical oxy-fluoride system. Although the CaO–CaF₂ system is generally accepted as a simple binary eutectic system, the published CaO and CaF₂ liquidus compositions are largely inconsistent with each other.⁴⁾

As a result, the eutectic composition is not well constrained: it lies between 17.5 and 26 mol% CaF₂ at about 1360°C.^{5–10)} Moreover, although very limited solubility of CaO in α -CaF₂ is reported at low temperature (between about 352 and 727°C),^{11–13)} no attempt to measure the solubility was made at high temperature. In order to resolve these problems, new phase diagram experiments are necessary.

As a part of a large research program to construct an accurate thermodynamic database for the oxy-fluoride system including CaO–Al₂O₃–SiO₂–MgO–FeO–MnO–Na₂O–Li₂O–K₂O–F for the applications of steel refining slag and continuous casting mould flux, key experiments and thermodynamic modeling were performed in the CaO–CaF₂ binary. In the present study, our new phase diagram on the CaO–CaF₂ binary system will be presented. In order to determine the phase diagram, high temperature equilibration/quenching experiments followed by the EDS chemical composition analysis and XRD phase determination were performed. In addition, DSC and TGA were used to determine the eutectic temperature and polymorphic transition temperature of CaF₂.

2. Experimental Method

2.1. Classical Equilibration Experiments

2.1.1. Preparation of Starting Materials

Reagent grade calcium carbonate (CaCO₃, ≥ 98.5 wt.%, Merck, Germany) and calcium fluoride (CaF₂, ≥ 97 wt.%, Merck, Germany) were used for preparing the starting mate-

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rials. The main impurity in CaCO_3 and CaF_2 is moisture. CaCO_3 was used instead of CaO due to its hygroscopic behavior. Appropriate proportions of starting materials were carefully weighed, mixed by a mechanical mixer for more than one hour and stored in a desiccator in batches of 3 to 10 g.

Due to the hygroscopic behavior of CaO and the possible moisture pickup from handling, the calcination of CaCO_3 to obtain CaO ($\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$) was conducted just before the experiments using only the required amount of premixed sample (20 to 40 mg). To prevent F loss during high temperature experiments, sealed Pt capsules were used. First, a partly welded (one side) Pt tube (10 mm length, 4.6 mm O.D., 0.3 mm wall thickness) was used as a container in the calcination process at 900°C in a box furnace for more than 4 hours. Sample weights were measured before and after calcination to confirm the completion of the reaction. After this, the samples were stored in a drying oven to cool down to 120°C and then in a desiccator to reach the room temperature. The materials were then crushed and packed in the capsule to remove the air gaps among the grains. The other end of the Pt capsule was then gently crimped to remove the air space as much as possible and then welded to ensure gas-tight conditions. Welding was performed with an electric arc welder and checked with an optical microscope before performing the experiments.

2.1.2. Experimental Procedure

A vertical one-atm tube furnace with MoSi_2 heating elements (Gero HTRV, Germany) was used for all phase equilibrium experiments. Temperatures were measured using type B thermocouples located at about 10 mm from the sample and independently controlled within $\pm 5^\circ\text{C}$ by an automated system which also logged the temperatures during the experiments.

For each experiment, several Pt capsules with different bulk compositions along the CaO – CaF_2 binary were bound together with thin Pt wire, which was held by a thin Pt wire. The pack of Pt capsules was then lowered from the top of the furnace to the hot zone. After the desired equilibration time at working temperature, the Pt wire was melted by an electric current, such that the capsules fell into a crucible filled with water in the bottom part of the furnace for rapid quenching. Samples that showed leakage during the experiment were rejected from analysis.

2.1.3. Analytical Methods

Samples from the first experiments were embedded in epoxy resin with the Pt capsule to observe the phase distribution in the capsule. The capsule was first pierced and then vacuum impregnated with epoxy resin to preserve the sample distribution during quenching. The sample was then cut with a diamond saw and polished with water-free lubricant. In the later experiments, the sample material was recovered from the Pt capsules and embedded in epoxy. All polished sections were prepared just before microscopic observations and microanalysis to avoid the hydration of CaO .

Phase recognition and composition analysis was conducted with a Field Emission Scanning Electron Microscope (FE-SEM, JEOL JSM 7001F, Japan) equipped with an Energy-dispersive X-ray spectrometer (EDS, Thermo Scientific,

USA) system. Based on preliminary analyses,¹⁴⁾ the optimal EDS conditions for compositional analyses of F-containing samples were obtained with an accelerating voltage of 7 kV and a measurement area of about $500\ \mu\text{m}^2$. To ensure consistency in the analytical results, other conditions such as the working distance (10 mm) and the aperture (3) were fixed. Data acquisition required 30 minutes per area and normally 5 to 10 areas were measured for each phase. In a sample, the identification and distribution of each phase was first made before selecting the measurement areas. The matrix correction was done with the Proza (Phi-Rho-Z) method and the background correction was performed manually to increase the analysis accuracy. Internal standards embedded with the samples were always used to minimize errors in the quantitative EDS analysis. The standards were wollastonite (O) and calcium fluoride (Ca and F). All the FE-SEM EDS data were processed with the PARC (PhASE Recognition and Characterization) technique, developed by Corus (Tata Steel Europe, The Netherlands). Details regarding the PARC technique can be found elsewhere.¹⁵⁾

Both SEM and optical microscopy (Imager Z1, Carl Zeiss, Germany) techniques were used for the phase distribution examination. X-Ray Diffraction (XRD, D8 Discover, Bruker, USA) was employed for the identification of crystal phases. Image analysis was performed using backscattered electron images analyzed with Axio-Vision software (Carl Zeiss, Germany).

2.2. Differential Scanning Calorimetry (DSC) and Thermo-gravimetric Analysis (TGA)

2.2.1. Materials Preparation

Reagent grade calcium oxide (CaO , 99.95 wt.%, Alfa Aesar, USA) and calcium fluoride (CaF_2 , 99.95 wt.%, Alfa Aesar, USA) were used for preparing the starting materials. Batches of 5 to 10 g were mixed in an agate mortar for one hour. Due to the hygroscopic character of CaO , mixing was performed in isopropyl alcohol to prevent moisture pickup from the air. The mixtures were then kept in a drying oven at 110°C for more than 12 hours to dry off the alcohol and cooled down to room temperature in a desiccator.

2.2.2. Experimental Procedure

DSC and TGA measurements were performed using a Jupiter STA 449 F3 thermal analyser (NETZSCH Instruments, Germany). Pt-Rh crucibles (6.8 mm O.D. with a capacity of $85\ \mu\text{l}$) with lids were used to carry 20 to 40 mg of sample for each run. The heating and cooling rates were $10\ \text{K min}^{-1}$ and an argon atmosphere with a gas flow rate of $20\ \text{ml min}^{-1}$ was used to avoid hydration of the sample. Temperature and sensitivity calibrations were conducted by using the phase transition temperature and enthalpy of melting of the following reference materials: biphenyl ($\text{C}_{12}\text{H}_{10}$), benzoic acid ($\text{C}_7\text{H}_6\text{O}_2$), rubidium nitride (RbNO_3), potassium perchlorate (KClO_4), caesium chloride (CsCl), potassium chromate (K_2CrO_4), barium carbonate (BaCO_3), and diopside ($\text{CaMgSi}_2\text{O}_6$).

F loss could not be avoided because the crucibles were not sealed. The composition change resulting from F loss was monitored by TGA in order to track the actual composition of the samples during experiments. The annealing temperature was always set to about $1\ 000^\circ\text{C}$ to remove the

moisture and homogenize the samples with minimum amount of F loss. Two to three heating and cooling cycles were run for each sample to obtain reliable thermal signal results. Due to F evaporation, the gas outlet was occasionally checked to keep the accuracy of the TGA balance because clogging can cause unstable TG signals.

3. Results and Discussion

After each equilibration and quenching experiment, the products were typically attached to the Pt capsule wall in the form of small lumps of materials (due to their surface tension) where all the equilibrium phases were homogeneously distributed. As an example, the homogeneity of the phase distribution can be seen in the back-scattered electron (BSE) image of samples L2 (held at 1 650°C above the solidus) and S4 (held at 1 250°C below the solidus) in Fig. 1.

All experimental result are summarized in Tables 1 to 4

Fig. 1. Backscattered electron (BSE) images of quenched samples showing examples of phase distribution in the capsules. (a) Sample L2 quenched from 1 650°C and (b) sample S4 quenched from 1 250°C.

Table 1. Experimental conditions and results of CaO and CaF₂ liquiii.

Sample	Composition (mol%)		Temperature (°C)	Duration (h)	Phases ¹	Liquid composition (mol%)		Error (mol%)
	CaO	CaF ₂				CaO	CaF ₂	
L1	30	70	1650	1	CaO + Liquid	23.8	76.2	6.76
L2	50	50	1650	1	CaO + Liquid	25.5	74.5	5.33
L3	20	80	1600	1	Liquid	23.5	76.5	2.39
L4	25	75	1600	1	CaO + Liquid	26.9	73.1	4.71
L5	50	50	1500	1	CaO + Liquid	22.2	77.8	3.82
L6	30	70	1390	2	CaO + Liquid	21.4	78.6	3.58
LS1	5	95	1390	2	CaF ₂ + Liquid	11.6	88.4	1.65

¹: The composition of solid CaO was determined to be pure CaO in all cases.

Table 2. Experimental conditions and results of sintered samples containing CaF₂ crystals.

Sample	Composition (mol%)		Temperature (°C)	Duration (h)	Phases	CaO/Pore in CaF ₂	Figure
	CaO	CaF ₂					
LS1	5	95	1390	2	CaF ₂ + Liquid	CaO	4 (a)
S8	10	90	1200	66	CaO + CaF ₂	Pore	4 (b)
S9	10	90	1400 (5 min), 1200	66	CaO + CaF ₂	Pore	4 (c)
S5	10	90	1500 (1 hr), 1200	84	CaO + CaF ₂	Pore	4 (d)

and presented in the phase diagram of Fig. 2.

3.1. The CaO and CaF₂ Liquidii

Experimental conditions and results for the CaO and CaF₂ liquidii are given in Table 1. Despite all the precautions taken to quench rapidly the capsules, all quenched liquid samples show small CaO quench crystals (CaO particles exsolved from liquid during the quenching of the samples).

Fig. 2. Experimental results of the CaO–CaF₂ system determined in the present study along with the phase diagram (solid lines calculated from the thermodynamic modeling).¹⁷⁾

Table 3. Experimental conditions and results for the CaO solubility in CaF₂.

Sample	Composition (mol%)		Temperature (°C)	Duration (h)	Phases ¹	CaF ₂ composition (mol%)		Error (mol%)
	CaO	CaF ₂				CaO	CaF ₂	
LS1	5	95	1390	2	CaF ₂ + Liquid	5.6	94.4	2.03
S1	3	97	1500 (1 h), 1300	86	CaF ₂	3.7	96.3	2.06
S2	5	95	1300	76	CaO + CaF ₂	4.8	95.2	2.77
S3	10	90	1300	24	CaO + CaF ₂	2.9	97.1	2.04
S4	10	90	1250	65	CaO + CaF ₂	4	96	2.61
S5	10	90	1500 (1 h), 1200	84	CaO + CaF ₂	4.8	95.2	2.11
S6	10	90	1050	260	CaO + CaF ₂	4.6	95.4	2.07
S7	10	90	1000	260	CaO + CaF ₂	2.9	97.1	2.06
S10*	10	90	1500 (1 h), 1200	84	CaO + CaF ₂	2.3	97.7	3.00

¹: The composition of solid CaO was determined to be pure CaO in all cases.

*: Analyzed using XRD.

Table 4. Experimental conditions and results for the eutectic and polymorphic transition temperatures determined by DSC and TGA.

Sample	Composition (mol%)		Solidus (°C)	Polymorphic transition (°C)
	CaO	CaF ₂		
D1	20	80	1361	1151
D2	10	90	1362	1142
D3(Pure CaF ₂)	0	100	1420 (fusion)	1146

The amount and distribution of exsolved CaO vary according to the equilibration temperature of the charge. The largest amount of exsolved CaO particles is observed and distributed more inhomogeneously at the highest equilibration temperatures for a given composition. Typical microstructures obtained for the CaF_2 -rich liquid are shown in Fig. 3. Usually, 5 areas of glass or glass + exsolved CaO were randomly selected to analyze the overall liquid composition; this is the case of sample L6 quenched from 1390°C in Fig. 3(b). However, 10 areas were analyzed for the samples equilibrated at the highest temperatures, such as sample L1 quenched from 1650°C in Fig. 3(a), because the distribution of exsolved phases was much more inhomogeneous than in low-temperature samples. The size of the analyzed area was about $477\text{ }\mu\text{m}^2$. In fact, Figs. 3 (a) and 3(b) are corresponding to the actual area analyzed for liquid composition of each sample. Fortunately, the primary crystalline CaO particles in equilibrium with the liquid are typically larger than about $20\text{ }\mu\text{m}$ in diameter, which can be easily distinguished from the exsolved CaO particles of less than $1\text{ }\mu\text{m}$ in diameter. There is no interference of the primary CaO particle for liquid analysis because all liquid + CaO samples contain large amount of liquid area (the initial compositions of all samples are closer to CaO liquidus than solid CaO).

Experimental results obtained for the liquid are shown on the phase diagram of Fig. 2. For the CaO liquidus, the error in liquid composition is relatively large (about 3 to 7%) due to the inhomogeneous nature of the exsolved CaO particles. Moreover, the initial composition of the samples might be slightly shifted toward the CaO-rich side of the phase diagram due to possible F loss during sample preparation. This can explain sample L4, where the liquid has almost the same composition as the starting material after the formation of primary CaO crystals. In the case of sample L3, no large primary CaO particles were observed, which indicates that the sample was fully liquid at 1600°C. It should also be noted that our CaO liquidus is very similar to the one of Ries and Schwerdtfeger,¹⁶⁾ who employed the EPMA technique on samples equilibrated in sealed Pt capsules like us. No trace of F solubility into solid CaO was detected in the samples. For the CaF_2 liquidus, only one experiment was performed. It corresponds to sample LS1 which contains 95 mol% CaF_2 equilibrated at 1390°C.

3.2. Solubility of CaF_2 in Solid CaO

The solubility of CaF_2 in CaO was determined using FE-SEM EDS. In order to get rid of the interference from CaF_2 -containing liquid or solid CaF_2 , CaO particles larger than $20\text{ }\mu\text{m}$

Fig. 3. BSE images of typical microstructures observed in quenched liquid samples. (a) Sample L1 quenched from 1650°C and (b) sample L6 quenched from 1390°C.

μm in diameter were considered for the analysis of CaF_2 solubility. The morphology of CaO particles was in a spherical shape both in CaO + Liquid or CaO + CaF_2 samples. No CaF_2 (all EDS analyses showed zero amount of F) was detected in solid CaO.

3.3. Solubility of CaO into Solid CaF_2

The microstructures observed in four CaF_2 crystals with different thermal histories are shown in Fig. 4. Experimental conditions and results of these four samples are summarized in Table 2. In the case of solid CaF_2 equilibrated with liquid (that is above the solidus temperature; Fig. 4(a), sample LS1), small exsolved CaO particles, which seems to have formed during the quenching process, are present in solid CaF_2 . In the sample equilibrated at sub-solidus temperature (Fig. 4(b), sample S8), no such exsolved CaO particles are visible but a significant amount of sintered pores (holes) in solid CaF_2 can be seen. When the samples are partially (Fig. 4(c), sample S9) or completely (Fig. 4(d), sample S5) melted and subsequently annealed at sub-solidus temperature, the shape of the holes in solid CaF_2 is different from that in the samples equilibrated only at sub-solidus temperature (Fig. 4(b)). Moreover, the size of the holes becomes smaller and smaller as the sample is more and more melted. From these observations, it is possible to conclude that the pores observed in solid CaF_2 are mainly due to an incomplete sintering process of the powder or shrinkage during quenching rather than exsolution of CaO from CaF_2 crystals. Consequently, the pores were excluded in the PARC analyses of all sub-solidus samples.

In order to confirm the accuracy of the FE-SEM EDS analysis using the PARC technique in the determination of the solubility of CaO in solid CaF_2 , the solubility was also determined by BSE image analysis and XRD on samples S5 and S10, respectively. Sample S10 underwent the same heat treatment as sample S5 (which is discussed above). The composition of the CaF_2 solid solution can be relatively well estimated by mass balance calculations by subtracting the

Fig. 4. BSE images of solid CaF_2 crystals with different thermal histories. (a) Equilibrated above the solidus, (b) equilibrated below the solidus, (c) partially melted and equilibrated below the solidus and (d) completely melted and equilibrated below the solidus.

Fig. 5. The solubility of CaO in CaF₂ at 1200°C analyzed by various techniques. The position of the symbols is slightly shifted according to the temperature axis to avoid superposition.

amount of CaO (in mol%), measured either by image analysis and XRD, from the initial amount of CaO (in mol%) of the starting material. Obviously, this calculation is only valid if the solubility of CaF₂ in solid CaO is zero, which is confirmed by FE-SEM EDS as discussed in section 3.2. Results are depicted in Fig. 5 along with the one obtained on sample S5 by FE-SEM EDS analysis using the PARC technique. As it can be seen in the figure, the solubility measured by the FE-SEM EDS/PARC method is close to the one determined by BSE image analysis while the value measured by XRD is slightly lower but still in agreement with the others if we consider the errors. Such a difference is expected from the XRD because the accuracy of the technique is typically $\pm 5\%$.

The accuracy of the FE-SEM EDS/PARC method being supported by two independent techniques (BSE image analysis and XRD), all the sub-solidus samples of our study were analyzed by this method. Results of these solubility measurements are summarized in Table 3 and shown in Fig. 2. The solubility of CaO in solid CaF₂ at sub-solidus temperatures ranges between 2.9 and 5.6 mol% between 1000 and 1390°C, respectively. In order to check the solubility of CaO in CaF₂, sample S1, which contains 97 mol% of CaF₂, was melted at 1500°C for 1 hour and then equilibrated at 1300°C for 86 hours. The sample showed only CaF₂ crystals and no CaO phase, which supports the noticeable solubility of CaO in CaF₂. According to the present experimental data, the maximum solubility of CaO in CaF₂ reaches about 5 mol% at the eutectic temperature, and decreases gradually with decreasing temperature. Furthermore, the change of solubility in CaF₂ seems to be continuous with temperature regardless of the CaF₂ structure (α or β) within the experimental error range. The dissolution behavior of CaO in α and β -CaF₂ is thus similar.

3.4. Temperatures of the Eutectic and the CaF₂ Polymorphic Transition

Temperatures of the CaO–CaF₂ eutectic and the α/β -CaF₂ transition were measured by DSC and TGA. Unfortunately, while equilibration experiments employed sealed Pt capsules to prevent F loss, DSC and TGA experiments used Pt crucibles and lids which did not prevent F loss. Fortunately, this problem had no impact on the results since the determi-

Fig. 6. DSC peaks of α/β -CaF₂ polymorphic transition and eutectic temperatures of sample D1.

nation of the eutectic and polymorphic transition temperatures are independent of the composition.

The samples were first heated up to about 1500°C and cooled down to about 1000°C where they were equilibrated for 2 to 3 hours and heated again to 1500°C for a second and third cycle. During the thermal cycles, the F loss was monitored by TGA and showed to be systematically significant above about 1360°C, the eutectic temperature determined by DSC. For example, the DSC analysis result for sample D1 is presented in Fig. 6. The whole results are given in Table 4 and depicted in the phase diagram of Fig. 2. The eutectic temperature was determined to be $1361 \pm 1^\circ\text{C}$, which is in good agreement with the previous studies: $1361 \pm 4^\circ\text{C}^{(8)}$ and $1360^\circ\text{C}^{(7)}$. The α/β -CaF₂ polymorphic transition was located at 1151 and 1142°C in the binary samples D1 (80 mol% CaF₂) and D2 (90 mol% CaF₂), respectively. The average of these two determinations gives $1146 \pm 5^\circ\text{C}$, which is the same as the polymorphic transition temperature of pure CaF₂ solid solution. The solubility of CaO has therefore no effect on the transition temperature of CaF₂, which indicates that the thermodynamics of CaO dissolution in α and β -CaF₂ follows the same Henrian solution behavior. Attempts to measure the CaO and CaF₂ liquidus temperatures in binary CaO–CaF₂ samples failed as the enthalpy of melting was too small to be recognized in the DSC signal.

3.5. Phase Diagram of the CaO–CaF₂ System

The lines in Fig. 2 depict the phase diagram calculated using the thermodynamic modeling⁽¹⁷⁾ based on the current experimental data and all reliable literature data for the phase diagram and thermodynamic properties. In the thermodynamic modeling, the liquid phase was treated as an ideal ionic solution and CaF₂ solid solution were modeled using the compound energy formalism considering the substitution of two F atoms with one O atom and vacancy. According to the optimization, the CaO–CaF₂ system is a simple binary eutectic system with the eutectic reaction $L(\text{CaO} = 15.3 \text{ mol}\%) \rightarrow \text{CaO}_{(\text{pure solid})} + \text{CaF}_{2(\text{solid solution with CaO} = 4.8 \text{ mol}\%)}$ occurring at 1362°C. The optimization using the thermodynamic modeling can be found elsewhere.⁽¹⁷⁾

4. Summary

Equilibration and quenching method was used with sealed Pt capsules to determine the positions of the CaO and CaF₂ liquidii and the solubility of CaO in solid CaF₂. The

solubility was measured by FE-SEM EDS analysis using the PARC technique and was supported by image analysis and XRD. In addition, DSC and TGA experiments were performed to locate the temperatures of the eutectic and the α/β -CaF₂ polymorphic transition.

For the first time, noticeable solubility of CaO in both α - and β -CaF₂ solids were observed above 1 000°C. The maximum solubility of CaO is about 5 mol% at 1 361°C, the eutectic temperature, while no solubility of CaF₂ in solid CaO is detected. The α/β -CaF₂ polymorphic transition temperature is located at $1\,146 \pm 5^\circ\text{C}$, which is the same temperature as pure CaF₂. Based on the thermodynamic optimization using the present CaO and CaF₂ liquidii and the eutectic temperature measurements, it is concluded that the CaO–CaF₂ phase diagram is a simple eutectic system with the eutectic reaction $L_{(\text{CaO} = 15.3 \text{ mol}\%)} \rightarrow \text{CaO}_{(\text{pure solid})} + \text{CaF}_{2(\text{solid solution with CaO} = 4.8 \text{ mol}\%)}$ occurring at 1 362°C.

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