Iron – Oxygen – Uranium

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Introduction

The Fe-O-U system is a key system in the disposal of nuclear waste where iron oxide is used with uranium waste and finds relevance in the prediction of high temperature phase behavior of corium. Two ternary compounds have been reported for the Fe-O-U system: $UFeO_4$ and UFe_2O_6 which seems to be stable only under high pressures [1978Col]. The experimental work is summarized in Table 1. The Fe-O-U ternary system was reviewed by [1989Rag]. [1964Eva] and [1983Smi] have constructed isothermal sections at different temperatures and partial pressures. [1973Buz] has reported the solubility of oxygen in (Fe,U) liquid alloys at 1600°C.

Binary Systems

The Fe-U and O-U binary systems are accepted from the critical assessments of [2003Cha] and [2004Che], respectively. A precise model of the solid and liquid oxide solutions taking into account the oxygen vacancies in the O-U system may be found in [2002Gue]. The O-U binary phase diagram from [2004Che] is presented in Fig. 1. The Fe-O phase diagram is accepted from the assessment by [1991Sun].

Solid Phases

The crystallographic data for the phases present in the Fe-O-U system and their ranges of stability are summarized in Table 2.

Invariant Equilibria

Table 3 lists the invariant reactions of the Fe-O-U ternary system from investigation of [1964Eva]. They have identified two ternary eutectic points which occur at oxygen partial pressures of 0.028 and 0.011 bar, respectively.

Isothermal Sections

[1989Rag] gave the Fe-O-U isothermal section at 400°C from the experimental investigations of [1983Smi]. This diagram, shown in Fig. 2, is compatible with the well known fact that Fe_3O_4 oxidizes into Fe_2O_3 at lower oxygen pressures than UO_2 oxidizes into U_4O_9. Unfortunately, neither [1964Eva] nor [1983Smi] took into account the ternary compound $UFeO_4$ obtained from the reaction:
$2U_3O_8+3Fe_2O \rightleftharpoons UFeO_4+0.5O_2$.

Temperature – Composition Sections

[1964Eva] have carefully investigated the equilibrium relationships between uranium and iron oxides as a function of oxygen pressure (586-21300 Pa) and temperature (1200-1460°C). Figures 3 to 8 show the projected isobaric sections under oxygen pressures of 21300 (air atmosphere), 7093, 3456, 1773, 892 and 586 Pa, respectively. It must be pointed out that the diagrams presented are not vertical sections because the phases in equilibrium are strongly dependent of the oxygen pressure. For instance, under air atmosphere Fe_2O_3, stable under 1415°C loses its oxygen to give Fe_3O_4 above that temperature as shown in Fig. 3. The transition $Fe_2O_3 \rightleftharpoons Fe_3O_4$ occurs at 1359, 1328, 1306, 1289 and 1273°C under 7093, 3456, 1773, 892 and 586 Pa of oxygen pressure, respectively. In the same way, the transition $U_3O_8 \rightleftharpoons UO_2$ occurs at 1448, 1385, 1358, 1316 and 1296°C under 7093, 3456, 1773, 892 and 586 Pa of oxygen pressure, respectively. The three phases UO_2-Fe_2O_3-Fe_3O_4 coexist in the solid state at 1248°C under 200 Pa of oxygen pressure.

Notes on Materials Properties and Applications

The ferric-ferrous buffer (mixture Fe_3O_4-Fe_2O_3) found naturally may be used to stabilize the state of oxidation IV of uranium [1983Smi].
Fe-U oxides can be used in an energetically efficient way as catalysts for the partial oxidation of propane and propene into formaldehyde which is an industrially important intermediate [2003Tay] in addition to the applications mentioned in the Introduction.

References

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Table 1: Investigations of the Fe-O-U Phase Relations, Structures and Thermodynamics

Reference	Method/Experimental Technique	Temperature/Composition/Phase Range Studied
[1964Eva]	Thermogravimetric analysis under controlled oxygen pressures	UO_2-U_3O_8-Fe_2O_3-Fe_3O_4, 1260-1460°C, 586 to 21300 Pa of oxygen pressure
[1973Buz]	Interaction parameters measurements	Liquid Fe-O-U alloy (< 10 mass% U, <2 mass% O), 1600°C

Reference	Method/Experimental Technique	Temperature/Composition/Phase Range Studied
[1978Col]	High pressure synthesis, X-ray diffraction	UFe_2O_6, 600°C, 3 GPa
[1983Smi]	X-ray diffraction	UO_2-U_3O_8-Fe_2O_3-Fe_3O_4, 400°C

Table 2: Crystallographic Data of Solid Phases

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
(αU) < 668	*oC*4 *Cmcm* αU	*a* = 285.37 *b* = 586.95 *c* = 495.48	at 25°C [Mas2]
(βU) 776 - 668	*tP*30 $P4_2/mnm$ βU	*a* = 1075.9 *c* = 565.6	at 25°C [Mas2]
(γU) 1135 - 776	*cI*2 $Im\bar{3}m$ W	*a* = 352.4	[Mas2]
(Fe) 1538 - 1394 < 912	*cI*2 $Im\bar{3}m$ W	*a* = 286.65 *a* = 293.15	at 25°C [Mas2] at > 1394°C [Mas2]
(γFe) 1394 - 912	*cF*4 $Fm\bar{3}m$ Cu	*a* = 364.67	at 25°C [Mas2]
Fe_2U < 1235	*cF*24 $Fd\bar{3}m$ Cu_2Mg	*a* = 705.5	[2003Cha]
FeU_6 < 829	*tI*28 *I*4/*mcm* MnU_6	*a* = 1024.99 *c* = 525.00	[2003Cha]
$Fe_{1-x}O$ (wüstite) 1422 - 569	*cF*8 $Fm\bar{3}m$ NaCl	 *a* = 431.0 *a* = 429.3	$0.05 < x < 0.12$ [1991Sun] $x = 0.05$ $x = 0.12$
Fe_3O_4 (r) < 580	*oP*56 *Pbcm* Fe_3O_4 (r)	*a* = 1186.8 *b* = 1185.1 *c* = 1675.2	[V-C2]
Fe_3O_4 (h) (magnetite) 1597 - 580	*cF*56 $Fd\bar{3}m$ $MgAl_20_4$	*a* = 839.6 *a* = 854.5	at 25°C at 1000°C [V-C2]
αFe_2O_3 (hematite) < 1451	*hR*30 $R\bar{3}c$ Al_2O_3	*a* = 503.42 *c* = 1374.83	at 600°C [Mas2, V-C2]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
βFe_2O_3	*cI*80 $Ia\bar{3}$ Mn_2O_3	*a* = 939.3	metastable phase [V-C2]
γFe_2O_3 (maghemite)	*tP*60 $P4_12_12$ Mn_5Si_2 (?)	*a* = 833.96 *c* = 832.21	metatable phase [V-C2]
UO_2 < 2852	*cF*12 $Fm\bar{3}m$ CaF_2	*a* = 547.0	from 62.7 to 66.7 at.% O [2004Che]
U_4O_9 < 1123	*cI*832 $I\bar{4}32$ or $I4_132$	*a* = 2176	[2004Che]
U_3O_8 < 1870	*oC*44 *Cmcm*	*a* = 706.9 *b* = 1144.5 *c* = 830.3	[2004Che]
UO_3 < 669	*cP*4 $Pm\bar{3}m$ ReO_3	*a* = 414.6	[2004Che]
* $UFeO_4$	*oP** *Pbcn*	*a* = 488.80 *b* = 1193.7 *c* = 511.0	[1989Rag]
* UFe_2O_6	*hP** $P\bar{3}1m$ $PbSb_2O_6$	*a* = 504.0 ± 0.1 *c* = 469.2 ± 0.1	[1978Col] High pressure phase (600°C, 3 GPa)

Table 3: Invariant Equilibria

Reaction	*T* [°C]	Type	Phase	Composition (at.%)		
				U	Fe	O
$L \rightleftharpoons U_3O_8 + Fe_2O_3 + Fe_3O_4$	1318	E_1	L	13.50	21.76	64.74
$L \rightleftharpoons U_3O_8 + UO_2 + Fe_3O_4$	1326	E_2	L	14.65	20.75	64.60

Fig. 1: Fe-O-U. Isothermal section at 400°C

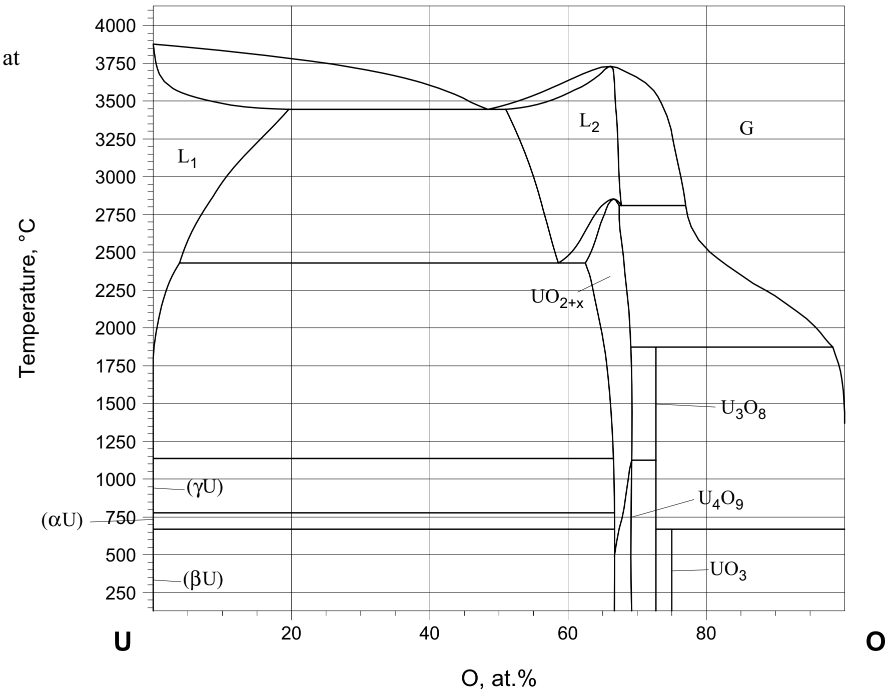

Fig. 2: Fe-O-U. Isothermal section at 400°C

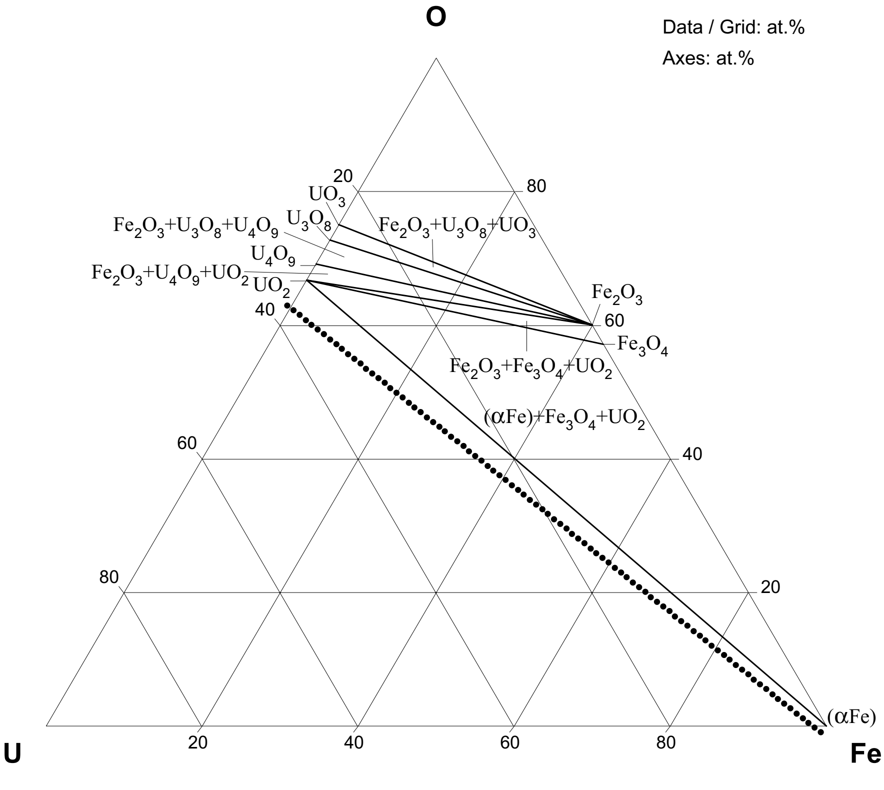

Fig. 3: Fe-O-U. Isobaric section under 21300 Pa of oxygen (1355 and 1415°C)

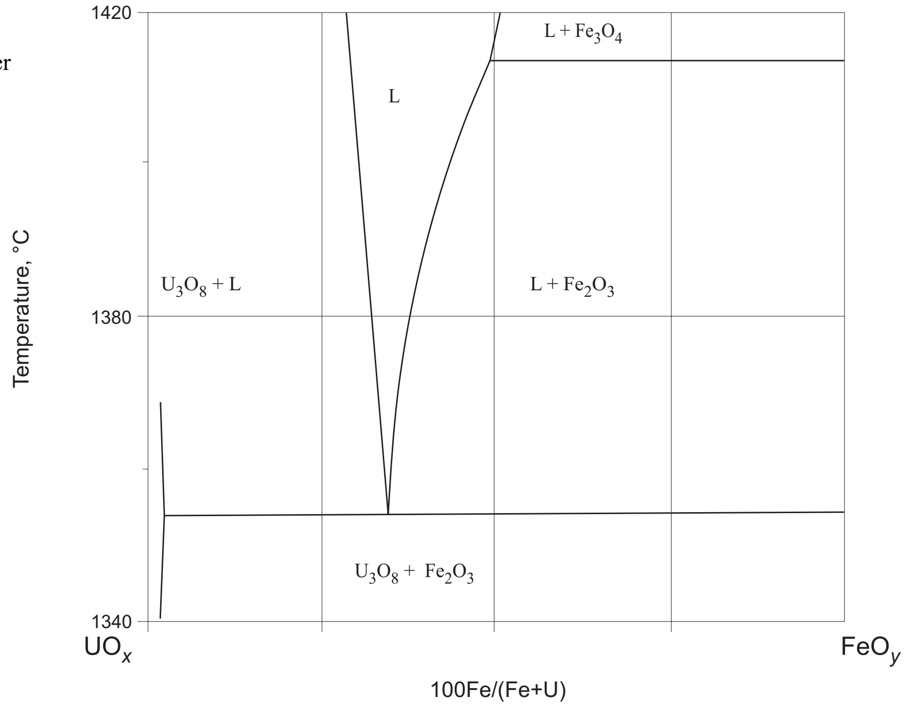

Fig. 4: Fe-O-U. Isobaric section under 7093 Pa of oxygen (1328, 1359 and 1448°C)

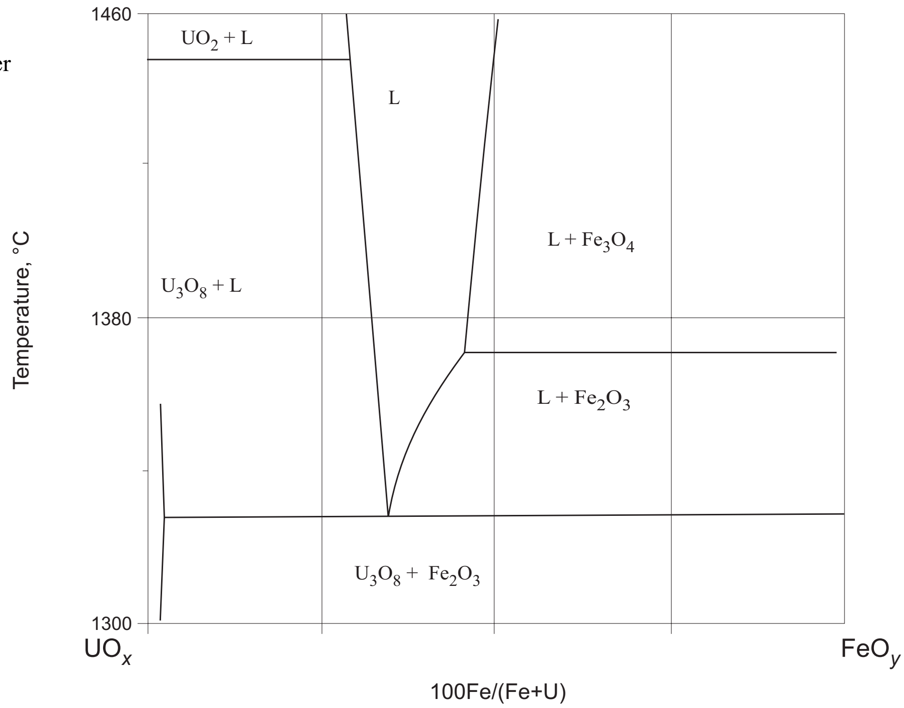

Fig. 5: Fe-O-U. Isobaric section under 3456 Pa of oxygen (1322, 1328 and 1385°C)

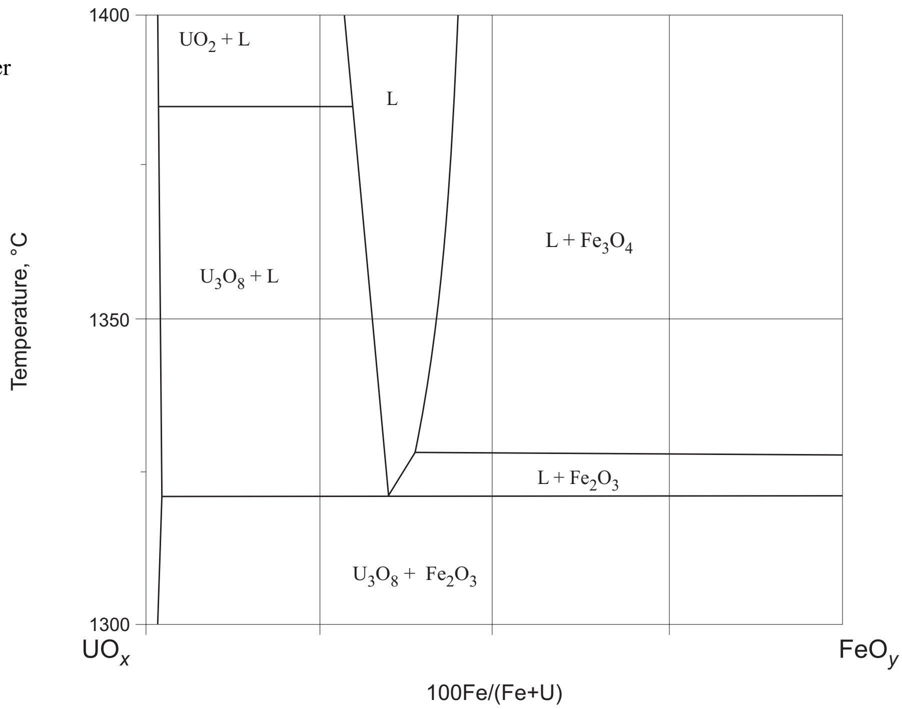

Fig. 6: Fe-O-U. Isobaric section under 1173 Pa of oxygen (1306, 1334 and 1358°C)

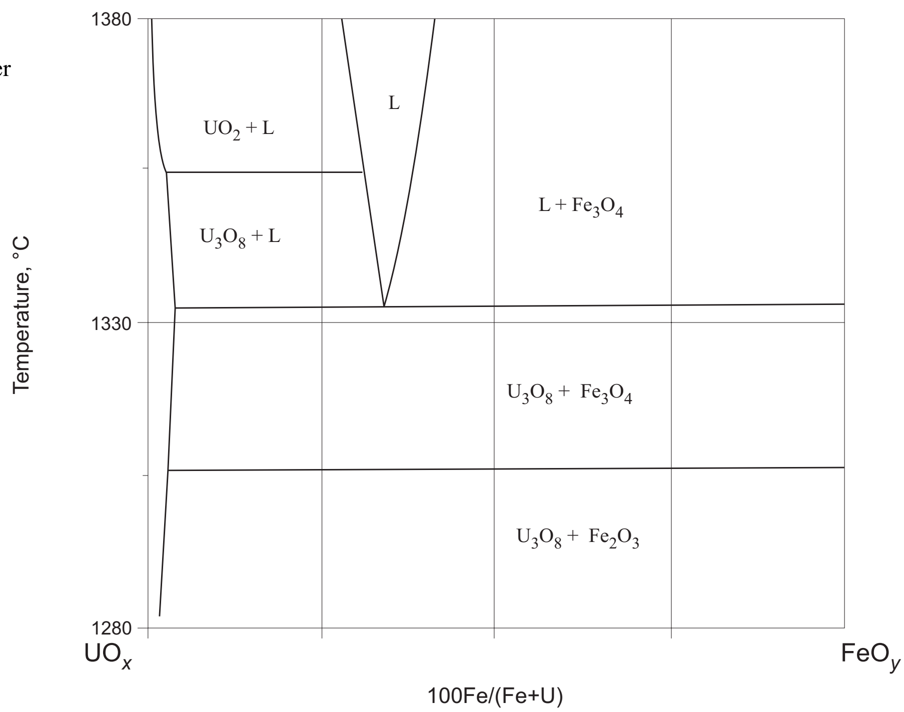

Fig. 7: Fe-O-U. Isobaric section under 892 Pa of oxygen (1289, 1316 and 1334°C)

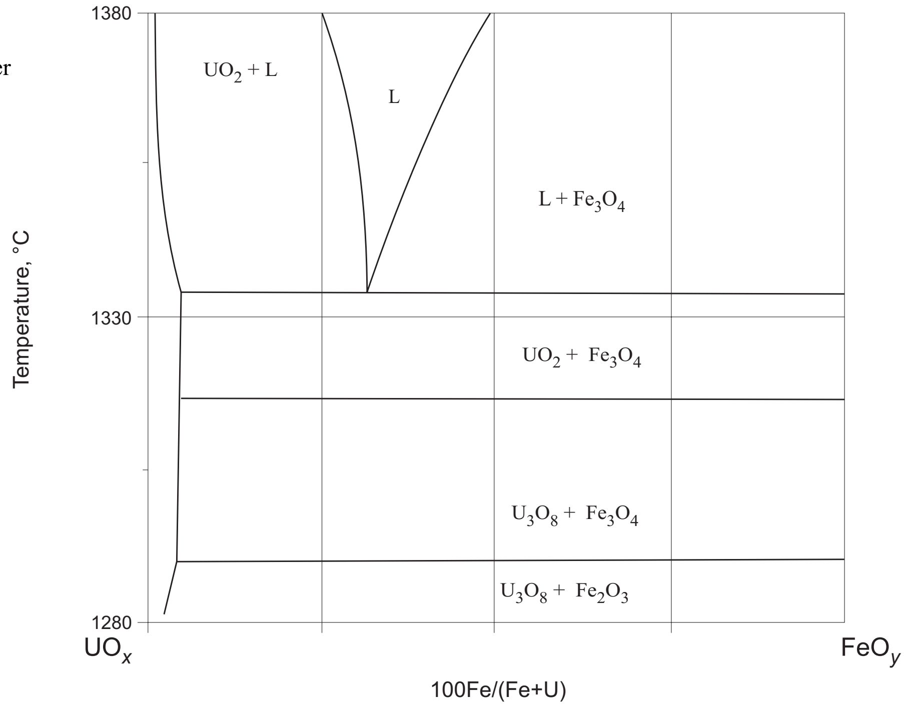

Fig. 8: Fe-O-U. Isobaric section under 586 Pa of oxygen (1273, 1296 and 1350°C)