화학공학의 역사
(원자폭탄과 분리공학)

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방사선

- 1900 도른: 알파,베타,감마선 발견
- 1900 퀴리: 베타선이 음전기, 알파선 보다 큰 투과력을 가짐을 발견
- 1906 라더포드: 알파선=헬륨 원자핵
- 1913 소디: 방사선 붕괴 법칙 발견

  라듐(원자번호 88, 질량수 226)이 알파 붕괴 되면 라돈(86,222)가 됨, 중성자가 베타 붕괴 되면 양성자가 되며 원자번호 1 증가

동위원소

- 1910 소디: 방사성 원소가 화학적 성질이 같고 질량수가 다름을 제시하고 동위원소라고 명명
- 1912 톰슨: 질량수 20, 22인 두종류의 Ne발견
- 1919 아스톤: 질량분석계로 기체 중의 동위원소 분리, 황(32,33,34), 염소(35,37), 규소 (28,29,30)
- 1912 까지 라더포드 그룹(소디, 한, 마이트너,---)에서 30개의 동위원소 보고

원자핵의 인공변환

- 1914 라더포드: 질소+알파입자->양성자+산소(17)
- 1932 콕크로프트: 리티움+양성자->2헬륨
- 1930년대: 200개의 안정한 동위원소, 40개의 방사선 동위원소 보고
- 초우라늄 원소의 제조: 1940 Np (U(238)+중성자->U(239)->Np(원자번호 93)+베타선), 1944 Am(95), 1944 Cm(96), 1949 Bk(97), Cf(98), 1953 Es(99), Fm(100), 1955 Md(101), 1957 No(102)

핵분열

- 1939 U(92,235)+중성자->Kr(36,84)+Ba(56,189)+중성자+에너지
- U(235): 연쇄반응 가능, 자연계에 0.7%
- U(238): 연쇄반응 방해, 99.3%
- 1942 페르미: 원자로 제작
- 1942 오크리지 연구소: U235 separation plant operation
- 1945 원자폭탄 실험

원자력의 평화적 이용

- 핵분열 반응속도의 조절과 원자력 발전
- 방사선 동위원소의 생물체 내에서 분포 실험: 방사선 인, 코발트 60, 요드 131
- 연대 측정: 1948 아르곤40 이용, 1947 탄소14 사용
- 핵연료의 분리:채굴->분쇄, 추출->yellow cake(U_3O_8) -> 정제, 농축(UO_2->UF_4->UF_6) ->U^{235} enrichment as UF_6

Uranium separation

- Yellow-colored glass, containing more than 1% uranium oxide and dating back to 79 A.D., has been found near Naples, Italy.
- Klaproth recognized an unknown element in pitchblende and attempted to isolate the metal in 1789. The metal apparently was first isolated in 1841 by Peligot.
- The earliest successful methods were electromagnetic isotope separation (EMIS), in which large magnets are used to separate ions of the two isotopes, and gaseous diffusion, in which the gas uranium hexafluoride (UF_6) is passed through a porous barrier material; the lighter molecules containing ^{235}U penetrate the barrier slightly more rapidly, and with enough stages significant separation can be accomplished.
- The first large-scale uranium enrichment facility, the Y-12 plant at Oak Ridge, Tennessee, used EMIS in devices called "calutrons." The process was abandoned in the United States because of its high consumption of electricity.

Uranium separation

- More efficient methods have been developed. The method in widespread use is the gas centrifuge in which UF 6 gas is whirled inside complex rotor assemblies and centrifugal force pushes molecules containing the heavier isotope to the outside.
- Manhattan Project scientists and engineers explored several uranium-enrichment technologies, and production plants employing three uranium-enrichment processes : electromagnetic isotope separation (EMIS), liquid thermal diffusion, and gaseous diffusion -- were constructed at Oak Ridge, Tennessee, during the period from 1943 to 1945.
- Centrifugation was tried, but the technology needed to spin a rotor at an appropriate speed was not then practical on an industrial scale.
- The aerodynamic separation processes developed in Germany and South Africa did not exist during World War II.

Thermal diffusion

- Thermal diffusion utilizes the transfer of heat across a thin liquid or gas to accomplish isotope separation. By cooling a vertical film on one side and heating it on the other side, the resultant convection currents will produce an upward flow along the hot surface and a downward flow along the cold surface.
- Under these conditions, the lighter 235 U gas molecules will diffuse toward the hot surface, and the heavier 238 U molecules will diffuse toward the cold surface.
- These two diffusive motions combined with the convection currents will cause the lighter 235 U molecules to concentrate at the top of the film and the heavier 238 U molecules to concentrate at the bottom of the film.
- The thermal-diffusion process is characterized by its simplicity, low capital cost, and high heat consumption. Thermal diffusion in liquid UF 6 was used during World War II to prepare feed material for the EMIS process. A production plant containing 2,100 columns (each approximately 15 meters long) was operated in Oak Ridge for less than 1 year.
- The thermal-diffusion plant in Oak Ridge was dismantled when the much more energy-efficient gaseous-diffusion plant began operation in the 1940.

Gas centrifuge

- The use of centrifugal fields for isotope separation was first suggested in 1919; but efforts in this direction were unsuccessful until 1934, when J.W. Beams and co-workers at the University of Virginia applied a vacuum ultracentrifuge to the separation of chlorine isotopes.
- Although abandoned midway through the Manhattan Project, the gas centrifuge uranium-enrichment process has been highly developed and used.
- Centrifugal force causes the heavier 238 UF6 molecules to tend to move closer to the wall than the lighter 235 UF6 molecules, thus partially separating the uranium isotopes.

Aerodynamic separation

- Vortex tubes were used by South Africa in their Helikon vortex separation process. The gas is injected tangentially into a chamber with special geometry that further increases its rotation to a very high rate, causing the isotopes to separate.
- The method is simple because vortex tubes have no moving parts, but energy intensive, about 50 times greater than gas centrifuges.
- A similar process, known as *jet nozzle*, was created in Germany, with a demonstration plant built in Brazil, and they went as far as developing a site to fuel the country's nuclear plants.

Chemical and Ion Exchange

- The chemical-exchange process, developed by the French, is commonly referred to as CHEMEX. It uses the exchange reaction that takes place between two valence states (U 3+ and U 4+) of uranium ions in aqueous solution.
- Isotopic enrichment results from the tendency of 238 U to concentrate in the U 3+ compound while 235 U concentrates in the U 4+ compound.
- It is therefore possible to obtain enriched uranium by removing the U 4+ ions with an organic solvent that is immiscible with the aqueous phase (concentrated hydrochloric acid).
- Several possible extractants are available; however, tributyl phosphate (TBP), the choice of the French, is typically used. TBP is diluted with an aromatic solvent, and this organic phase moves countercurrent to the aqueous phase through a series of pulsed columns.

Separation Engineering

- Equilibrium stage operation: distillation, extraction
- Nonequilibrium rate operation: thermal diffusion, chromatography
- Separation process development is crucial for uranium enrichment.