

Table 1. Molecular weights after fractionation of the nonvolatile degradation product of  $\beta$ -carotene by means of thin-layer chromatography.

| Fraction | $R_F$ | Molecular weight |
|----------|-------|------------------|
| 1        | 0.9   | $384 \pm 1$      |
| 2        |       | $476 \pm 8$      |
| 3        |       | $590 \pm 6$      |
| 4        |       | $442 \pm 20$     |
| 5        |       | $462 \pm 5$      |
| 6        |       | $431 \pm 3$      |
| 7        |       | $517 \pm 13$     |
| 8        |       | $580 \pm 16$     |
| 9        |       | $622 \pm 12$     |
| 10       |       | $731 \pm 36$     |
| 11       |       | $762 \pm 23$     |
| 12       | 0.08  | $983 \pm 24$     |

petroleum ether and do not move either with the solvent used for developing the thin-layer chromatogram or during elution of the fractions from the silica gel.

The molecular weights of the fractions were determined in chloroform with a Mechrolab osmometer (Table 1). From the determination of the iodine values by Kaufmann's micro-method (6) it is possible to calculate that the fractions contain between two and five double bonds.

The results indicate that the mechanism of degradation of  $\beta$ -carotene without solvent is evidently the same as that in solution, the same volatile products being identifiable in each case. Whereas toluene, *m*- and *p*-xylene, and

2,6-dimethylnaphthalene are formed by cyclization of the polyene chain, the  $\beta$ -ionone ring is involved in the formation of ionene. This was confirmed by experiments which were carried out on canthaxanthin, a carotenoid with a carbonyl group in positions 4 and 4' of the  $\beta$ -ionone rings. After comparable thermal degradation no ionene could be identified among the volatile decomposition products.

Nothing is yet known about the structure of the high-molecular-weight, nonvolatile products derived from the thermal degradation of  $\beta$ -carotene, either as the crystalline substance at 240°C or in the benzene solution at 188°C.

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## Periodic Phenomena Observed with Spherical Particles in Horizontal Pipes

**Abstract.** A thin layer of spherical particles resting on the bottom of a round pipe was observed to form into essentially equally spaced clumps or islands at fluid velocities only slightly greater than those required to initiate particle movement. This phenomenon appeared to be similar to dune formation in open channels since the ratio of the square of the stream velocity,  $U$ , and the product of the gravitational constant,  $g_v$ , and the island wavelength,  $\lambda$ , was correlated by the same function of island height and velocity, particle diameter, and fluid depth regardless of whether the flow was through a closed conduit or an open channel.

During studies of the transport of suspensions of spherical particles in round horizontal pipes by flowing water (1), it was observed (2) that if the fluid velocity was adjusted to a value only slightly greater than that required to initiate particle movement, then the particles grouped into clumps or islands within seconds to minutes after the flow rate had been adjusted. The clumps of particles were spaced periodically along the bottom of the pipe

and moved slowly downstream. Although the formation of periodic sand dunes or ripples commonly occurs during sediment transport in flow in which there is a free surface (3–5) (streams and flumes), it is apparently not widely known that such a phenomenon can occur in horizontal round pipes full of running water. In 1953 a theory of dune formation in an open channel was proposed which required the existence of water waves on a free fluid

surface (6). In those few instances in which the occurrence of dunes in pipe flow has been mentioned, little or no data were reported on dune characteristics or flow conditions (7). Because of the paucity of experimental data and the opportunity afforded for clarification of the mechanism of dune formation, an extensive study was made over a range of pipe diameters ( $D$ ) from 2.5 to 10 cm, mean particle diameters ( $D_p$ ) from 50 to 565  $\mu$ , and particle densities ( $\rho_p$ ) of 2.65 and 1.09 g/cm<sup>3</sup> in equipment described previously (1). The advantage of using a round pipe rather than a flat-bed flume is that the island train formed in a pipe possesses well-defined, easily measured characteristics in contrast to the rather chaotic conditions often observed in flumes.

Typical shapes for the clumps or islands are shown in Fig. 1. In this figure the islands of island train I were formed by the use of glass beads 565  $\mu$  in diameter. The mean wavelength was 10 cm and the mean island velocity ( $u_i$ ) was 1.23 cm/sec when the mean stream velocity was 45.2 cm/sec. The islands of island train II were formed when glass beads 50  $\mu$  in diameter were used. The mean wavelength was 4.68 cm and the mean island velocity was 0.045 cm/sec when the mean stream velocity was 33 cm/sec.

In the early phases of the study, it was observed that the islands occurred only over a rather narrow range in mean stream velocities with a slight dependence on pipe diameter. (The mean stream velocity was always based on the pipe diameter). For example, this range was found to be roughly from 15 to 45 cm/sec for 100  $\mu$  glass beads and from 30 to 65 cm/sec for 565  $\mu$  glass beads; it was extremely difficult to form islands with glass beads greater than 750  $\mu$  in diameter. The range of flow conditions for which island formation was observed has been described in detail (8). Despite the narrow range in mean stream velocities, the island velocity  $u_i$  varied over a 500-fold range being roughly proportional to the fifth power of the mean stream velocity as observed by Liu (4) for ripple motion in open channel flow. In all cases the island velocity was less than 5 percent of the mean stream velocity.

Comparison of the data for the configuration of islands formed in closed pipes with values—obtained from the literature—for dunes in open flumes,

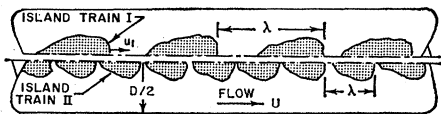


Fig. 1. Diagram of glass-bead "islands" formed in horizontal pipes with turbulently flowing liquids.

ivers, shoals, and ocean channels showed many similarities. The ratio of island (or dune) wavelength to height,  $\lambda/H$ , was 9 to 40 in the present study and 13 to 37 in Simon's work (5) with an open flume, while in an extensive study of large sand waves in rivers, shoals, and ocean channels, Jordan (9) reported that 70 percent of the sand waves had  $\lambda/H$  values in the range 35 to 60 with an average value of 45 to 50. The ratio of island (or dune) height to pipe diameter or channel depth,  $H/D$ , averaged 0.2 for water depths from 2.5 cm to 75 m (4, 5, 9, 10) with extreme values of 0.06 to 0.7 reported in some instances. These ratios serve to define what is meant by islands or dunes in this report.

The mechanism responsible for the initial formation of sediment into islands or dunes and the factors affecting their wavelength, height, and forward motion is poorly understood. Attempts to develop a general theory are complicated by the many forms of bed roughness described in the literature (6, 11) and the fact that such phenomena can occur in a channel in which ebb and flow conditions occur (12). Among the mechanisms proposed for sediment-wave initiation are the increase in local fluid velocities due to vortices trailing from irregularities in the bed surface (13) and the roll-up of vortex sheets generated at the bed-fluid interface (4). Attempts to describe the bed configuration usually start with a two-dimensional potential flow model (6, 11, 14) and incorporate empirically determined features where appropriate.

It has been established (8) that the minimum velocity for island formation in pipes corresponds to the velocity at which a single particle is transported without saltation and without obviously rolling or bouncing on the bottom of the pipe (15). Thus, when liquid flows over a thin, smooth layer of particles on the bottom of a pipe at velocities equal to or greater than the minimum required for island formation, there is a net upward force on the top layer of particles such that

the slightest perturbation in flow will dislodge particles permitting island formation to begin. Since island formation was observed to occur almost simultaneously over the 6-m length of glass pipe available in this study, it is postulated that the perturbation required to dislodge particles from the virtually fluidized top layer of particles is simply the fluctuation in pressure at the wall known to exist (16) in a turbulently flowing fluid.

Once particle movement has begun, the formation of islands or dunes seems to be primarily an inertial phenomenon similar to Helmholtz instability which occurs in parallel flow at the interface of two fluids of different density (17). The fact that in this particular case the lower "fluid" consists of a liquid-particle mixture is presumably not of primary importance, since the nature of such a mixture merely introduces a time lag in the perturbation equation to account for the time required to cause incipient fluidization of the second layer of particles as the upper layer is transported to form the characteristic dune or island pattern. For small-wave height, when the velocity of one medium is small relative to that of the other medium and if surface tension effects are neglected, the Helmholtz equation reduces approximately to:

$$\frac{U^2}{g_L \lambda} \left/ \left( \frac{\rho_p - \rho}{\rho} \right) \right. = \frac{1}{2\pi} \quad (1)$$

In reality, discrepancies are observed between Eq. 1 and experimental data. These are attributed to viscous effects, flow separation, and to fluid turbulence (17). Since the present data gave val-

ues always less than  $1/2\pi$  when substituted in the left side of Eq. 1, the right side was modified to the form:

$$(1/2\pi) \tanh [f(u_i, H, D, D_p)].$$

The tanh function was chosen because for small values of the argument it reduces to the argument and for large values of the argument it approaches unity. The empirical function,  $f$ , was evaluated graphically. For small values of the argument,  $f$ , the result was:

$$\frac{U^2}{g_L \lambda} \left/ \left( \frac{\rho_p - \rho}{\rho} \right) \right. = \frac{1}{2\pi} \left[ \frac{1}{4} \left( \frac{u_i^2}{g_L H} \right) \left( \frac{D}{H} \right)^{5/3} \left( \frac{D}{D_p} \right)^{2/3} \right]^{0.205} \quad (2)$$

as shown in Fig. 2. Although the value of the left side was always less than  $1/2\pi$ , it approached  $1/2\pi$  more rapidly than predicted from the tanh function. While the tanh function is completely arbitrary, this might also be due to the fact that the island velocity was sufficiently large to require the complete Helmholtz expression rather than the simplified form of Eq. 1.

The extensive data given by Simons *et al.* (5) on sand-dune formation in a 2.4-m wide flume (that is, a channel with a free liquid surface) are shown as open diamonds in the lower left portion of Fig. 2. The average depth was used as the diameter term and the mean stream velocity was based on this depth. As can be seen, the present data overlap the flume data and the flume data appear to follow the same trend as do the data for pipes full of running water. This is particularly

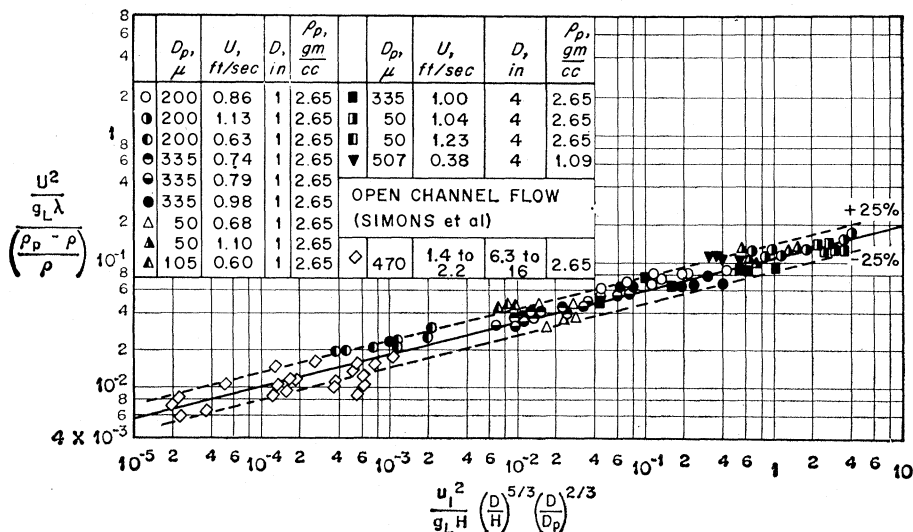


Fig. 2. Correlation of periodic phenomenon observed in suspension transport in horizontal pipes and open channels.

noteworthy since the depth of water in the flume was 1.5 to 4 times the largest pipe diameter studied and the dune wavelength was 1.23 to 2.4 m, or from 9 to 17 times longer than the maximum wavelength observed in the present study. These limited data indicate that sand waves in closed pipes, open flumes, rivers, and channels are closely related phenomena and hence any theories must account for the data from all these systems.

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#### Radioactive Particle in Sediment from the Columbia River

**Abstract.** A "hot particle" containing only fission product radioactivity is comprised of a number of characteristics that make the particle unusual and its origin uncertain.

A single particle with fission product radioactivity in the millimicrocurie range has been isolated from sediments in the Columbia River. High activity,

large size, and apparent lack of fractionation make it quite unlike other reported individual fallout particles (1). The particle was isolated from sediments taken 23 July 1963, near Blacklock, Oregon, about 210 km down river from the nuclear reactors at Hanford, Washington.

Surface sediments were collected from beneath about 2 m of fast-flowing water. The samples were then air-dried and passed through a 200-mesh screen. Seven 5-g portions of sediment (particle size less than 74  $\mu$  in diameter) were counted in the well of a 5- by 5-inch NaI(Tl) crystal. The signal from the detector was resolved with a 256-channel pulse-height analyzer.

Unusually high activity was noted in one of the samples (No. 5, Table 1). The single particle was isolated by repeated divisions of the highly active portion. Fission product radioactivity of the particle was equivalent to that found in about 200 g of average sediment from the same location.

When examined under a microscope, the particle, 11 by 25  $\mu$  in size, appeared colorless and isotropic except for several small, poorly defined anisotropic inclusions. One large inclusion was brown. The particle itself was highly angular and had at least three cleavage planes. Adams *et al.* (2) describe similar particles and inclusions associated with surface shots at the Nevada test site.

Neutron-induced radioactivity in sediments results from activation of trace elements in river water that is used to cool nuclear reactors at Hanford. However, very few fission products arise from this source (3). Neutron-induced radionuclides appear to be more evenly distributed throughout sediments than fission products. Scandium-46, for example, showed only small variations between portions of the same sample (Table 1). This would seem to indicate that fission products are associated with relatively fewer sediment particles than are neutron-induced isotopes.

The gamma spectrum of sample No. 5 (Fig. 1A) contains peaks due to neutron-induced radionuclides such as zinc-65, cobalt-60 and scandium-46. When the particle was isolated from the sediment and recounted, its spectrum (Fig. 1B) showed peaks only for the fission products zirconium-95-niobium-95, ruthenium-103, and cerium-141-144. The slight increase in fission product activity after separation is due to

Table 1. Fission product activity and neutron-induced activity in 5-g samples of Columbia River sediment.

| Sample No.                   | Fission product<br>Zr <sup>95</sup> -Nb <sup>95</sup><br>(pc/g) | Neutron-induced<br>Sc <sup>46</sup><br>(pc/g) |
|------------------------------|---|---|
| 1                            | 33  | 44  |
| 2                            | 22  | 40  |
| 3                            | 82  | 40  |
| 4                            | 11  | 34  |
| 5                            | 760   | 34  |
| 6                            | 22  | 47  |
| 7                            | 14  | 38  |
| Mean $\pm$ S.D. 31 $\pm$ 24* |   | 40 $\pm$ 4.5                                  |

\* No. 5 is not included.

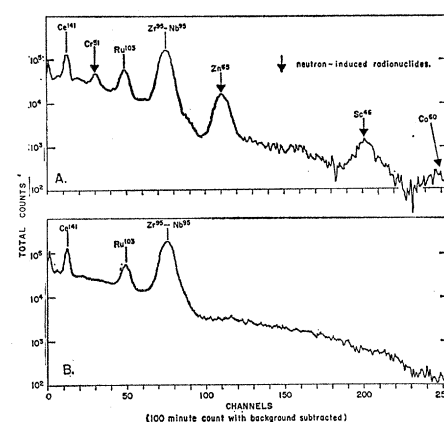


Fig. 1. A, Spectrum of 5-g sediment sample. Peaks indicated for scandium-46 and cobalt-60 are "sum peaks." B, Spectrum of "hot" particle after isolation (one channel equals 10 kev).

changes in geometry and self-absorption (4). Equations of Rock *et al.* (5), for changes with time in the apparent half-life of the Zr<sup>95</sup>-Nb<sup>95</sup>, were used to set early April 1963 as the approximate date for the formation of the particle. No Russian tests were reported from December 1962 to June 1963. However, underground tests were conducted at the Nevada site during this period (6). A test was reportedly conducted in the Sahara Desert by the French government on 18 March (7).

A number of collections were made at four other stations on the river between Hanford and the ocean, but no similar "hot particle" was found. Measurements of fallout radionuclides in marine plankton and of filter samples from Oregon rivers and from rain water have failed to reveal anomalous particles; that is, dividing our samples generally resulted in a corresponding